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Supplementary Materials for

Asymmetric copper-catalyzed C-N cross-couplings induced by visible light

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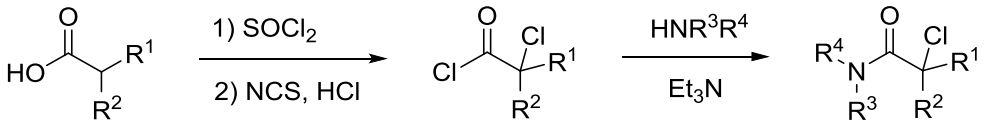
I. General Information

All manipulations of air-sensitive materials were carried out in oven-dried glassware using standard Schlenk or glovebox techniques under an N_2 atmosphere. Unless otherwise noted, chemicals were purchased from commercial suppliers and used as received. CH_2Cl_2, THF, and toluene were purified and dried using a solvent-purification system that contained activated alumina. Indoline (Aldrich), NEt_3 (EMD), $SOCl_2$ (Alfa), and SO_2Cl_2 (Acros) were distilled prior to use. Carbazole (Aldrich) and 3-methylindole (Aldrich) were recrystallized. Ligand (*S*)-**L*** was purchased from Strem (>99.9% ee) and used without further purification. Ligand (*R*)-**L*** was purchased from Strem (>98.6% ee) and was purified on preparative HPLC in the P-oxide form using a Daicel CHIRALPAK® AD column (80% *i*-PrOH/hexanes, 10.0 mL/min; (*S*)-**L***-oxide: 8.6 min, (*R*)-**L***-oxide: 24.6 min). The enantiopure ligand (>99.9% ee) was then obtained by reduction in analogy to a reported procedure (*30*).

^{1}H and ^{13}C NMR data were collected on a Bruker 400 MHz or a Varian 500 MHz spectrometer at ambient temperature unless otherwise noted. HPLC analyses were carried out on an Agilent 1100 Series system, using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 µm). ATR-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. Blue LED lamps (32 W; Kessil H150 Blue) were used to irradiate the reaction mixtures.

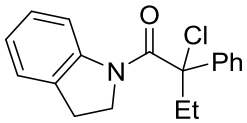
II. Preparation of Electrophiles

These procedures have not been optimized.



Representative procedure A for the synthesis of α-chloro amides: This is based on previously published procedures (*31, 32*). The carboxylic acid (25 mmol) was dissolved in $SOCl_2$ (7.25 mL, 100 mmol), and the resulting solution was heated at reflux at 80 °C for 30 min with vigorous stirring ($CaCl_2$ drying tube). The mixture was allowed to cool to r.t., and then *N*-chlorosuccinimide (8.34 g, 63 mmol), $SOCl_2$ (5 mL), and HCl (concentrated; 4 drops) were added. The resulting mixture was heated at 90 °C for 2.5 h. The mixture was then allowed to cool to r.t., the precipitate was removed by filtration, and the solvent was removed by evaporation. The resulting liquid residue was distilled into an ice-cooled flask.

Next, triethylamine (4.2 mL, 30 mmol) and the α-chloro acid chloride were added dropwise to a solution of a secondary amine (20 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The stirring was continued at 0 °C for 15 min and then at r.t. for 3 h. Next, an aqueous solution of HCl (1 M; 50 mL) was added, and the organic layer was separated. The organic phase was washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum.



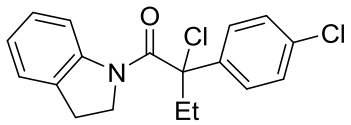
2-Chloro-1-(indolin-1-yl)-2-phenylbutan-1-one. The title compound was prepared from 2-phenylbutyric acid and indoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (88% yield over 2 steps). The enantiomers of the title compound can be separated by preparative HPLC on a Daicel CHIRALPAK® AD column (3% *i*-PrOH/ hexanes, 10 mL/min, internal diameter 20 mm, column length 250 mm, particle size 5 μm).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.42 – 7.28 (m, 3H), 7.28 – 7.19 (m, 1H), 7.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.05 (td, *J* = 7.4, 1.1 Hz, 1H), 4.17 (ddd, *J* = 10.9, 9.6, 6.5 Hz, 1H), 3.06 (ddd, *J* = 11.0, 9.7, 6.6 Hz, 1H), 2.93 (ddd, *J* = 16.1, 9.5, 6.7 Hz, 1H), 2.73 (ddd, *J* = 15.9, 9.6, 6.6 Hz, 1H), 2.53 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.30 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.86 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 144.0, 139.0, 131.7, 128.7 (2C), 128.1, 127.5, 126.0 (2C), 124.6, 124.5, 118.3, 76.6, 49.2, 37.8, 28.8, 8.8;

FT-IR (ATR) 2965, 1656, 1477, 1460, 1445, 1120, 861, 761, 751, 697 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{18}H_{19}ClNO$: 300.1150, found: 300.1140.



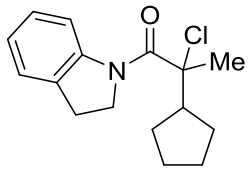
2-Chloro-2-(4-chlorophenyl)-1-(indolin-1-yl)butan-1-one. The title compound was prepared from 2-(4-chlorophenyl)butanoic acid and indoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (34% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.27 – 7.19 (m, 1H), 7.15 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.06 (td, *J* = 7.4, 1.1 Hz, 1H), 4.17 (ddd, *J* = 10.9, 9.6, 6.6 Hz, 1H), 3.10 (ddd, *J* = 10.9, 9.7, 6.5 Hz, 1H), 2.95 (ddd, *J* = 16.0, 9.6, 6.5 Hz, 1H), 2.77 (ddd, *J* = 15.9, 9.7, 6.6 Hz, 1H), 2.51 (dq, *J* = 14.5, 7.2 Hz, 1H), 2.26 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 143.8, 137.8, 134.1, 131.6, 129.0, 127.6, 127.4, 127.3, 124.6, 118.3, 75.9, 49.3, 37.7, 28.8, 8.7;

FT-IR (ATR) 2973, 2935, 1649, 1477, 1384, 1334, 1092, 1012, 816, 759 cm^{-1};

HRMS (ESI) *m/z* $(M–Cl)^+$ calcd for $C_{18}H_{17}ClNO$: 298.0993, found: 298.0990.



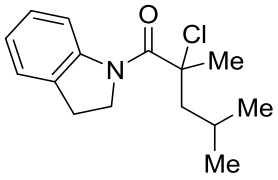
2-Chloro-2-cyclopentyl-1-(indolin-1-yl)propan-1-one. The title compound was prepared from 2-cyclopentylpropanoic acid and indoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (32% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 7.26 (tq, *J* = 6.8, 0.9 Hz, 2H), 7.11 (td, *J* = 7.3, 1.1 Hz, 1H), 4.62 (ddd, *J* = 10.8, 8.8, 6.6 Hz, 1H), 4.50 (ddd, *J* = 10.8, 9.0, 7.7 Hz, 1H), 3.27 – 3.10 (m, 2H), 2.99 – 2.86 (m, 1H), 2.01 (ddtt, *J* = 12.6, 8.9, 6.1, 3.6 Hz, 1H), 1.85 (s, 3H), 1.81 – 1.47 (m, 7H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 144.4, 131.6, 127.4, 124.5, 124.4, 118.7, 74.4, 50.6, 48.4, 29.5, 28.9, 28.1, 26.2, 25.9, 25.4;

FT-IR (ATR) 2939, 2861, 1637, 1595, 1479, 1386, 1369, 1333, 1265, 1067, 904, 751, 712, 690 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{16}H_{21}ClNO$: 278.1306, found: 278.1311.



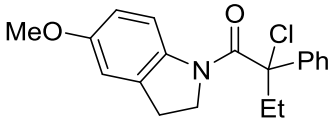
2-Chloro-1-(indolin-1-yl)-2,4-dimethylpentan-1-one. The title compound was prepared from 2,4-dimethylpentanoic acid and indoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (37% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.17 (m, 1H), 7.26 (ddt, *J* = 7.9, 6.8, 0.9 Hz, 2H), 7.11 (td, *J* = 7.3, 1.1 Hz, 1H), 4.76 (ddd, *J* = 10.7, 9.2, 6.2 Hz, 1H), 4.31 (ddd, *J* = 10.7, 9.3, 7.4 Hz, 1H), 3.30 – 3.08 (m, 2H), 2.25 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.13 (dd, *J* = 14.4, 5.3 Hz, 1H), 1.96 (s, 3H), 1.93 – 1.82 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 144.2, 131.6, 127.5, 124.5, 124.4, 118.6, 70.3, 50.4, 50.0, 29.8, 29.4, 25.9, 24.6, 23.3;

FT-IR (ATR) 2963, 2870, 1635, 1596, 1476, 1393, 1377, 1259, 1171, 1068, 889, 750 672 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{15}H_{21}ClNO$: 266.1306, found: 266.1309.



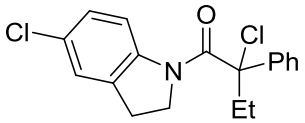
2-Chloro-1-(5-methoxyindolin-1-yl)-2-phenylbutan-1-one. The title compound was prepared from 2-phenylbutyric acid and 5-methoxyindoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (76% yield over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.35 – 7.28 (m, 1H), 6.76 (ddt, *J* = 8.9, 2.8, 0.8 Hz, 1H), 6.70 (ddd, *J* = 2.5, 1.4, 0.9 Hz, 1H), 4.15 (ddd, *J* = 11.0, 9.6, 6.4 Hz, 1H), 3.78 (s, 3H), 3.05 (ddd, *J* = 11.0, 9.6, 6.6 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.75 – 2.65 (m, 1H), 2.53 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.29 (dq, *J* = 14.4, 7.2 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 156.9, 139.2, 137.6, 133.3, 128.7, 128.0, 126.0, 118.9, 111.9, 110.8, 76.5, 55.8, 49.3, 37.7, 29.0, 8.8;

FT-IR (ATR) 2933, 2833, 1640, 1594, 1485, 1385, 1267, 1191, 1032, 859, 841, 752, 699 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{19}H_{21}ClNO_2$: 330.1255, found: 330.1250.



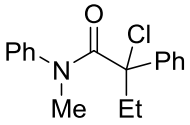
2-Chloro-1-(5-chloroindolin-1-yl)-2-phenylbutan-1-one. The title compound was prepared from 2-phenylbutyric acid and 5-chloroindoline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (76% yield over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 1H), 7.19 (ddt, *J* = 8.7, 2.3, 0.8 Hz, 1H), 7.09 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.18 (ddd, *J* = 11.0, 9.7, 6.5 Hz, 1H), 3.06 (ddd, *J* = 11.0, 9.7, 6.7 Hz, 1H), 2.96 – 2.86 (m, 1H), 2.76 – 2.66 (m, 1H), 2.51 (dq, *J* = 14.5, 7.2 Hz, 1H), 2.28 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 142.7, 138.8, 133.5, 129.4, 128.8, 128.2, 127.4, 125.9, 124.7, 119.1, 76.4, 49.3, 37.7, 28.6, 8.7;

FT-IR (ATR) 2972, 2931, 1657, 1468, 1374, 1329, 1169, 862, 836, 753, 699 cm^{-1};

HRMS (ESI) *m/z* $(M–Cl)^+$ calcd for $C_{18}H_{17}ClNO$: 298.0993, found: 298.0980.



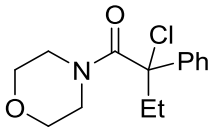
2-Chloro-*N*-methyl-*N*,2-diphenylbutanamide. The title compound was prepared from 2-phenylbutyric acid and *N*-methylaniline following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless oil (72% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 6.62 (m, 10H), 3.11 (br s, 3H), 2.46 (dt, *J* = 14.5, 7.1 Hz, 1H), 2.24 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.75 (br s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.8, 128.5, 127.6, 127.1, 125.7, 75.6, 40.9, 37.9, 8.6;

FT-IR (ATR) 2975, 2937, 1652, 1594, 1492, 1445, 1363, 1273, 748, 695 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{17}H_{19}ClNO$: 288.1150, found: 288.1162.



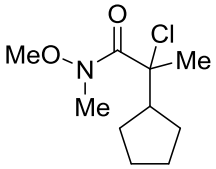
2-Chloro-1-morpholino-2-phenylbutan-1-one. The title compound was prepared from 2-phenylbutyric acid and morpholine following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished as colorless oil (78% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.14 (m, 5H), 3.65 – 2.45 (m, 4H), 3.33 – 3.15 (m, 2H), 3.00 – 2.75 (m, 2H), 2.26 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.07 (dq, *J* = 14.4, 7.2 Hz, 1H), 0.67 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 139.7, 128.7 (2 C), 128.1, 125.6 (2 C), 74.8, 66.8, 65.8, 47.8, 43.7, 38.1, 8.8;

FT-IR (ATR) 2972, 2920, 2857, 1644, 1443, 1425, 1270, 1237, 1111, 970, 864, 852, 750, 700 cm^{-1};

HRMS (ESI) *m/z* $(M–Cl)^+$ calcd for $C_{14}H_{18}NO_2$: 232.1338, found: 232.1346.



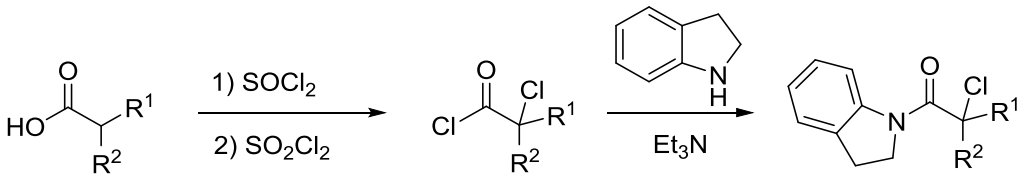
2-Chloro-2-cyclopentyl-*N*-methoxy-*N*-methylpropanamide. The title compound was prepared from 2-cyclopentylpropanoic acid and *N*,*O*-dimethylhydroxylamine·HCl following procedure A. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless oil (31% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.23 (s, 3H), 2.93 – 2.82 (m, 1H), 1.87 – 1.78 (m, 1H), 1.72 (s, 3H), 1.69 – 1.48 (m, 6H), 1.48 – 1.32 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 73.1, 60.8, 47.5, 34.4, 28.6, 28.0, 26.1, 25.9, 24.9;

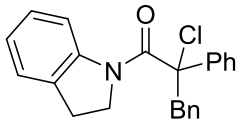
FT-IR (ATR) 2950, 2869, 1653, 1456, 1377, 1198, 998, 733, 642 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{10}H_{19}ClNO_2$: 220.1099, found: 220.1099.



Representative procedure B for the synthesis of α-chloro amides: This is based on previously published procedures (*31, 33*). The carboxylic acid (5.0 mmol) was dissolved in $SOCl_2$ (1.5 mL, 20 mmol), and the resulting solution was heated at reflux for 30 min with vigorous stirring ($CaCl_2$ drying tube). SO_2Cl_2 (4.1 g, 50 mmol) was added via a dropping funnel over 2 h at 85 °C, and then the mixture was heated at reflux for an additional 24 h. Next, the reaction mixture was allowed to cool to r.t., and the excess $SOCl_2$ and SO_2Cl_2 were removed by distillation.

Next, triethylamine (1.04 mL, 7.5 mmol) and the α-chloro acid chloride were added dropwise to a solution of indoline (560 μL, 5.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The stirring was continued at 0 °C for 15 min and then at r.t. for 3 h. Next, an aqueous solution of HCl (1 M; 20 mL) was added, and the organic layer was separated. The organic phase was washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum.



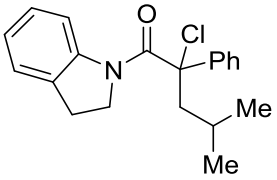
2-Chloro-1-(indolin-1-yl)-2,3-diphenylpropan-1-one. The title compound was prepared from 2-chloro-2,3-diphenylpropanoyl chloride following procedure B. The product was purified by flash chromatography on silica gel (0% → 10% Et_2O/hexanes), which furnished a colorless solid (60% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.23 – 7.16 (m, 2H), 7.17 – 7.12 (m, 2H), 7.11 – 7.03 (m, 3H), 6.74 – 6.66 (m, 2H), 4.15 (ddd, *J* = 10.9, 9.6, 6.3 Hz, 1H), 3.78 (d, *J* = 14.1 Hz, 1H), 3.62 (d, *J* = 14.0 Hz, 1H), 3.05 (ddd, *J* = 10.9, 9.6, 6.9 Hz, 1H), 2.94 (ddd, *J* = 16.2, 9.5, 6.8 Hz, 1H), 2.73 (ddd, *J* = 15.9, 9.6, 6.3 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 144.0, 138.2, 135.1, 131.9, 131.7, 128.5, 128.3, 127.6, 127.3, 126.8, 126.4, 124.63, 124.60, 118.4, 75.0, 49.9, 49.3, 28.8;

FT-IR (ATR) 3026, 1648, 1478, 1384, 1338, 1261, 953, 756, 699, 633 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{23}H_{21}ClNO$: 362.1312, found: 362.1306.



2-Chloro-1-(indolin-1-yl)-4-methyl-2-phenylpentan-1-one. The title compound was prepared from 4-methyl-2-phenylpentanoic acid following procedure B. The product was purified by flash chromatography on silica gel (0% → 8% Et_2O/hexanes), which furnished a colorless solid (52% yield over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 7.26 – 7.19 (m, 1H), 7.17 – 7.09 (m, 1H), 7.04 (td, *J* = 7.4, 1.1 Hz, 1H), 4.16 (ddd, *J* = 10.8, 9.5, 6.3 Hz, 1H), 3.03 (ddd, *J* = 10.7, 9.6, 6.8 Hz, 1H), 2.93 (ddd, *J* = 16.1, 9.6, 6.7 Hz, 1H), 2.72 (ddd, *J* = 15.8, 9.6, 6.3 Hz, 1H), 2.50 – 2.37 (m, 1H), 2.33 – 2.22 (m, 1H), 1.72 (pdd, *J* = 6.7, 5.4, 4.5 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.50 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 144.1, 139.2, 131.6, 128.8, 128.2, 127.5, 126.1, 124.6, 124.4, 118.4, 75.9, 52.7, 49.2, 28.8, 24.9, 24.4, 24.3;

FT-IR (ATR) 2956, 2868, 1656, 1599, 1479, 1387, 1338, 1266, 754, 701 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{20}H_{23}ClNO$: 328.1463, found: 328.1471.

III. Asymmetric Photoinduced, Copper-Catalyzed C–N Cross-Couplings

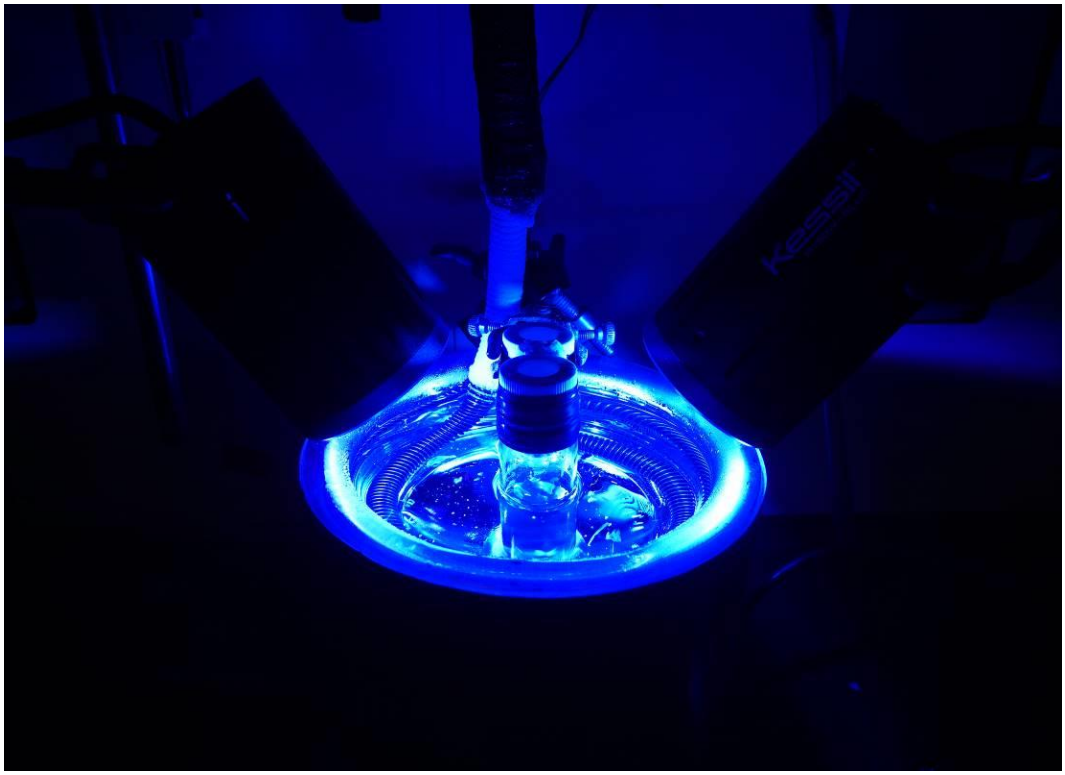


Fig. S1. Picture of the reaction setup, running two reactions in parallel.

General Procedure A and General Procedure B can be used interchangeably.

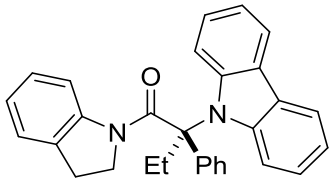
General Procedure A (glovebox-free). A stock solution of the catalyst was prepared by vigorously stirring CuCl (4.9 mg, 0.050 mmol) and (*S*)-**L*** (21.3 mg, 0.060 mmol) in toluene (10.0 mL) at 60 °C for 30 min under a nitrogen atmosphere. An oven-dried 40 mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and then backfilled with nitrogen. The carbazole or indole nucleophile (0.50 mmol) and LiO*t*-Bu (60.0 mg, 0.75 mmol) were added to the vial, and then the vial was placed under vacuum and refilled with nitrogen (three cycles). Next, toluene (17 mL) was added, and the resulting mixture was stirred for 5 min. Then, the catalyst (1.0 mL of the stock solution) was added, and the reaction mixture was stirred at r.t. for 20 min. The alkyl chloride (0.60 mmol) was added to an oven-dried 4 mL vial, the vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles). Toluene (2.0 mL) was added, and the resulting solution was transferred to the reaction mixture via syringe. The reaction mixture was degassed by applying three freeze-pump-thaw cycles. The reaction vial was backfilled with nitrogen, detached from the Schlenk line, and the holes in the septum were covered with grease. The vial was placed ~5 cm from two 32 W blue LED lamps, and the reaction mixture was irradiated at –40 °C for 16 h under a nitrogen atmosphere. Next, the mixture was passed through a

short plug of silica (eluant: Et_2O; monitored by TLC), and the resulting solution was concentrated under vacuum and purified by flash chromatography (hexanes/Et_2O).

A second run was performed using (*R*)-**L***.

General Procedure B (glovebox). In a nitrogen-filled glovebox, a stock solution of the catalyst was prepared by vigorously stirring CuCl (4.9 mg, 0.050 mmol) and (*S*)-**L*** (21.3 mg, 0.060 mmol) in toluene (10.0 mL) for 30 min; gentle heating by a heat gun facilitated the dissolution of the components. The carbazole or indole nucleophile (0.50 mmol) and LiO*t*-Bu (60.0 mg, 0.75 mmol) were added to a 40 mL vial, followed by a stir bar and toluene (17 mL). The mixture was stirred for 5 min, and then the stock solution of the catalyst (1.0 mL) was added, and stirring was continued for 20 min. The alkyl chloride (0.60 mmol) was dissolved in toluene (2.0 mL) and added to the reaction mixture. The vial was sealed with a PTFE-lined septum cap, the joint was wrapped with electrical tape, and the vial was taken out of the glovebox. The vial was placed ~5 cm from two 32 W blue LED lamps, and the reaction mixture was irradiated at –40 °C for 16 h under a nitrogen atmosphere. Next, the mixture was passed through a short plug of silica (eluant: Et_2O; monitored by TLC), and the resulting solution was concentrated under vacuum and purified by flash chromatography (hexanes/Et_2O).

A second run was performed using (*R*)-**L***.



(*S*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2B, Entry 1). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 193 mg (90% yield), 94% ee. Second run: 196 mg (91% yield), 93% ee.

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in hexanes of a sample synthesized with (*S*)-**L***.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 6.2 min (minor), 7.7 min (major).

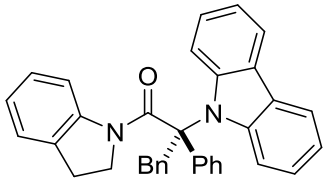
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (dt, *J* = 8.2, 0.7 Hz, 1H), 8.14 – 8.11 (m, 2H), 7.60 – 7.56 (m, 2H), 7.36 – 7.31 (m, 3H), 7.27 – 7.18 (m, 7H), 7.10 – 7.02 (m, 2H), 3.76 (ddd, *J* = 10.8, 9.3, 4.0 Hz, 1H), 3.24 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.11 (dt, *J* = 10.8, 9.3 Hz, 1H), 2.92 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.72 – 2.60 (m, 1H), 2.57 (ddd, *J* = 15.5, 9.2, 4.0 Hz, 1H), 0.69 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 144.0, 141.3, 137.9, 131.9, 128.8, 128.0, 127.9, 127.4, 125.6, 124.6, 124.5, 124.3, 120.1, 120.0, 119.1, 113.6, 74.2, 49.3, 32.3, 29.4, 10.5;

FT-IR (ATR) 2933, 1647, 1595, 1476, 1445, 1374, 1334, 1315, 1261, 1178, 1027, 748, 723 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{30}H_{27}N_2O$: 431.2118, found: 431.2112;

$[\alpha]^{25}_D$ (94% ee) = –27.1° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2,3-diphenylpropan-1-one (Fig. 2B, Entry 2). The title compound was synthesized according to General Procedure B from carbazole (66.9 mg, 0.40 mmol) and 2-chloro-1-(indolin-1-yl)-2,3-diphenylpropan-1-one (173.7 mg, 0.48 mmol). The product was purified by flash chromatography (0% → 10% Et_2O/hexanes). Colorless solid. First run: 149 mg (76% yield), 96% ee. Second run: 154 mg (78% yield), 91% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 7.6 min (minor), 13.9 min (major).

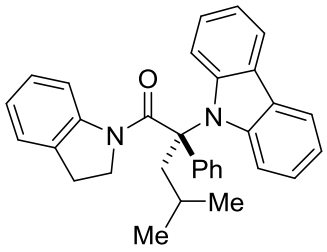
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (dt, *J* = 8.2, 0.8 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.77 – 7.68 (m, 2H), 7.46 – 7.35 (m, 3H), 7.33 – 7.27 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.13 – 7.04 (m, 4H), 6.97 (s, 2H), 6.80 (dt, *J* = 8.7, 4.3 Hz, 1H), 6.69 (d, *J* = 4.3 Hz, 4H), 4.80 (d, *J* = 13.5 Hz, 1H), 4.01 (d, *J* = 13.5 Hz, 1H), 3.77 (ddd, *J* = 10.7, 7.8, 5.0 Hz, 1H), 3.32 (dt, *J* = 10.7, 9.3 Hz, 1H), 2.59 – 2.46 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 144.1, 141.0, 136.5, 135.7, 131.8, 131.0, 128.9, 128.0, 127.8, 127.3, 127.0, 126.4, 124.9, 124.5, 124.3, 124.1, 119.65, 119.56, 119.0, 113.8, 74.9, 49.5, 42.6, 29.3;

FT-IR (ATR) 2955, 1652, 1596, 1540, 1476, 1455, 1375, 1335, 1314, 1211, 1031, 748, 723 cm^{-1};

HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{35}H_{29}N_2O$: 493.2280, found: 493.2280;

$[\alpha]^{25}_D$ (96% ee) = +46.8° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-4-methyl-2-phenylpentan-1-one (Fig. 2B, Entry 3). The title compound was synthesized according to General Procedure B from carbazole (66.9 mg, 0.40 mmol) and 2-chloro-1-(indolin-1-yl)-4-methyl-2-phenylpentan-1-one (157.4 mg, 0.48 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 150 mg (82% yield), 99% ee. Second run: 149 mg (81% yield), 99% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 0.7 mL/min); retention times for compound obtained using (*S*)-**L***: 6.5 min (minor), 7.6 min (major).

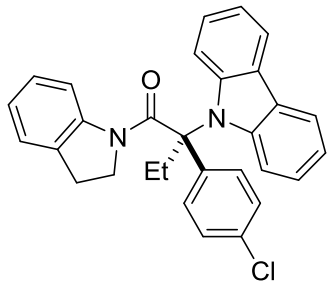
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.1 Hz, 1H), 8.17 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.72 – 7.63 (m, 2H), 7.55 – 7.14 (m, 10H), 7.13 – 7.03 (m, 2H), 3.82 (ddd, *J* = 10.8, 9.2, 3.4 Hz, 1H), 3.22 (dd, *J* = 14.2, 3.7 Hz, 1H), 3.05 (q, *J* = 9.9 Hz, 1H), 2.81 (dd, *J* = 14.1, 5.9 Hz, 1H), 2.65 (dt, *J* = 15.3, 9.5 Hz, 1H), 2.55 (ddd, *J* = 15.4, 9.1, 3.4 Hz, 1H), 1.80 (dqd, *J* = 13.1, 6.6, 3.7 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.22 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 144.0, 140.9, 138.1, 131.8, 128.7, 127.7, 127.6, 127.3, 125.3, 124.4, 124.3, 124.2, 120.0, 119.8, 119.0, 74.2, 49.4, 47.0, 29.3, 25.3, 25.0, 23.5;

FT-IR (ATR) 2955, 1652, 1595, 1489, 1446, 1375, 1313, 1211, 1163, 748, 724 cm^{-1};

HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{32}H_{31}N_2O$: 459.2431, found: 459.2435;

$[\alpha]^{25}_D$ (99% ee) = –36.7° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-2-(4-chlorophenyl)-1-(indolin-1-yl)butan-1-one (Fig. 2B, Entry 4). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-2-(4-chlorophenyl)-1-(indolin-1-yl)butan-1-one (200.5 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 196 mg (84% yield), 95% ee. Second run: 200 mg (86% yield), 90% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 7.4 min (minor), 9.6 min (major).

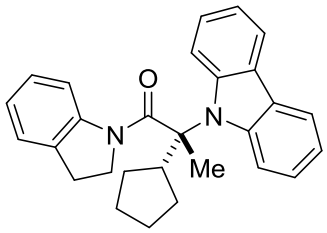
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dt, *J* = 8.1, 0.8 Hz, 1H), 8.17 (dd, *J* = 7.1, 2.7 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.23 (m, 7H), 7.14 – 7.06 (m, 2H), 3.85 (ddd, *J* = 10.6, 9.4, 3.7 Hz, 1H), 3.25 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.03 – 2.91 (m, 2H), 2.81 – 2.68 (m, 1H), 2.59 (ddd, *J* = 15.6, 9.2, 3.7 Hz, 1H), 0.81 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 143.8, 140.9, 137.2, 133.7, 131.6, 130.0, 128.0, 127.4, 125.8, 124.6, 124.4, 124.2, 120.12, 120.08, 118.9, 113.3, 73.7, 49.1, 32.2, 29.2, 10.4;

FT-IR (ATR) 2957, 1650, 1598, 1476, 1446, 1370, 1209, 1091, 838, 747, 721 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{30}H_{26}ClN_2O$: 465.1728, found: 465.1726;

$[\alpha]^{25}_D$ (95% ee) = –69.9° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*R*)-2-(Carbazol-9-yl)-2-cyclopentyl-1-(indolin-1-yl)propan-1-one (Fig. 2B, Entry 5). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-2-cyclopentyl-1-(indolin-1-yl)propan-1-one (166.7 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). White solid. First run: 169 mg (83% yield), 97% ee. Second run: 172 mg (84% yield), 98% ee.

X-ray quality crystals were obtained by slow diffusion of pentane into a saturated solution in benzene of a sample synthesized with (*S*)-**L***.

The ee was determined by HPLC on a Daicel CHIRALPAK® IB column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 6.2 min (major), 7.0 min (minor).

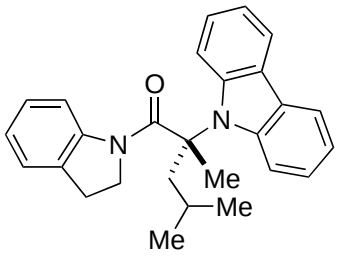
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 – 8.45 (m, 1H), 8.21 – 8.08 (m, 2H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.32 (q, *J* = 6.3 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.09 – 7.01 (m, 2H), 3.81 (ddd, *J* = 10.9, 9.7, 4.0 Hz, 1H), 3.61 – 3.50 (m, 1H), 2.90 – 2.79 (m, 1H), 2.50 – 2.46 (m, 1H), 2.45 (s, 3H), 2.43 – 2.30 (m, 2H), 1.81 – 1.63 (m, 3H), 1.48 (d, *J* = 3.3 Hz, 1H), 1.42 – 1.30 (m, 2H), 0.91 – 0.82 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 144.0, 140.7, 139.7, 131.2, 127.3, 126.1, 124.3, 124.1, 123.7, 120.5, 119.7, 119.4, 118.1, 112.5, 111.7, 69.8, 47.7, 47.6, 29.1, 28.9, 27.7, 26.3, 24.1, 19.9.

FT-IR (ATR) 2959, 1645, 1595, 1476, 1443, 1391, 1375, 1314, 1222, 747, 726 cm^{-1};

HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{28}H_{29}N_2O$: 409.2280, found: 409.2297;

$[\alpha]^{25}_D$ (97% ee) = +289° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*R*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2,4-dimethylpentan-1-one (Fig. 2B, Entry 6). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2,4-dimethylpentan-1-one (159.5 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 181 mg (91% yield), 89% ee. Second run: 179 mg (90% yield), 85% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® OD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 5.3 min (major), 9.5 min (minor).

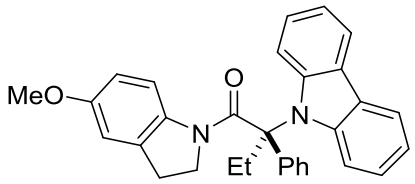
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.16 – 8.02 (m, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.37 – 7.30 (m, 1H), 7.29 – 7.17 (m, 3H), 7.05 – 6.96 (m, 2H), 3.54 (d, *J* = 11.9 Hz, 1H), 2.89 – 2.72 (m, 2H), 2.50 (ddd, *J* = 15.0, 9.5, 4.1 Hz, 1H), 2.37 (dd, *J* = 14.4, 4.2 Hz, 5H), 1.68 (hd, *J* = 6.6, 4.2 Hz, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.27 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 143.9, 140.7, 139.8, 131.1, 127.3, 126.2, 124.3, 124.1, 123.7, 120.5, 119.9, 119.7, 119.5, 118.1, 111.9, 111.8, 67.8, 47.4, 45.8, 28.9, 25.6, 24.4, 23.8;

FT-IR (ATR) 2954, 1640, 1595, 1477, 1454, 1375, 1316, 1220, 1075, 750, 723 cm^{-1};

HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{27}H_{29}N_2O$: 397.2280, found: 397.2270;

$[\alpha]^{25}_D$ (89% ee) = +202° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-1-(5-methoxyindolin-1-yl)-2-phenylbutan-1-one (Fig. 2B, Entry 7). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-1-(5-methoxyindolin-1-yl)-2-phenylbutan-1-one (197.9 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 15% Et_2O/hexanes). Colorless solid. First run: 213 mg (94% yield), 92% ee. Second run: 208 mg (90% yield), 92% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 10.2 min (minor), 14.1 min (major).

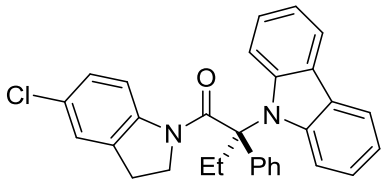
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.9 Hz, 1H), 8.21 – 8.13 (m, 2H), 7.66 – 7.60 (m, 2H), 7.42 – 7.33 (m, 3H), 7.31 – 7.09 (m, 6H), 6.82 (ddd, *J* = 8.7, 2.1, 1.3 Hz, 1H), 6.70 (dd, *J* = 2.6, 1.2 Hz, 1H), 3.82 (s, 4H), 3.30 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.14 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.95 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.67 (dtt, *J* = 15.6, 9.2, 1.1 Hz, 1H), 2.57 (ddd, *J* = 15.6, 9.2, 3.9 Hz, 1H), 0.73 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 156.9, 141.2, 137.9, 137.4, 133.4, 128.7, 127.9, 127.7, 125.5, 124.2, 120.0, 119.8, 119.6, 113.6, 111.7, 110.6, 73.9, 55.6, 49.4, 32.1, 29.4, 10.4;

FT-IR (ATR) 2927, 1642, 1594, 1488, 1445, 1374, 1297, 1181, 1031, 861, 748, 724 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{31}H_{29}N_2O_2$: 461.2224, found: 461.2220;

$[\alpha]^{25}_D$ (92% ee) = –27.5° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-1-(5-chloroindolin-1-yl)-2-phenylbutan-1-one (Fig. 2B, Entry 8). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-1-(5-chloroindolin-1-yl)-2-phenylbutan-1-one (200.5 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 10% Et_2O/hexanes). Colorless solid. First run: 213 mg (91% yield), 96% ee. Second run: 206 mg (89% yield), 96% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 9.1 min (minor), 11.6 min (major).

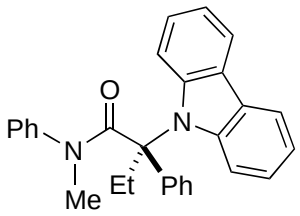
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.7 Hz, 1H), 8.21 – 8.14 (m, 2H), 7.66 – 7.59 (m, 2H), 7.43 – 7.34 (m, 3H), 7.33 – 7.11 (m, 7H), 7.08 (dt, *J* = 2.3, 1.2 Hz, 1H), 3.82 (ddd, *J* = 10.8, 9.4, 4.1 Hz, 1H), 3.29 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.15 (dt, *J* = 10.9, 9.3 Hz, 1H), 2.97 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.67 (dtt, *J* = 15.7, 9.3, 1.1 Hz, 1H), 2.58 (ddd, *J* = 15.7, 9.3, 4.1 Hz, 1H), 0.75 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 142.5, 141.0, 137.6, 133.7, 129.5, 128.7, 128.0, 127.9, 127.3, 125.6, 124.5, 124.2, 120.1, 120.0, 119.8, 113.2, 74.0, 49.4, 32.1, 29.0, 10.4;

FT-IR (ATR) 2936, 1652, 1593, 1465, 1444, 1367, 1315, 1210, 1164, 819, 748, 723 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{30}H_{26}ClN_2O$: 465.1728, found: 465.1725;

$[\alpha]^{25}_D$ (96% ee) = –16.4° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-*N*-methyl-*N*,2-diphenylbutanamide (Fig. 2B, Entry 9). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-*N*-methyl-*N*,2-diphenylbutanamide (172.7 mg, 0.60 mmol). 3.0 mL of the stock solution of the catalyst were used (3.0 mol% CuCl). The product was purified by flash chromatography (0% → 10% Et_2O/hexanes). Colorless solid. First run: 162 mg (78% yield), 94% ee. Second run: 168 mg (80% yield), 93% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 6.5 min (major), 9.6 min (minor).

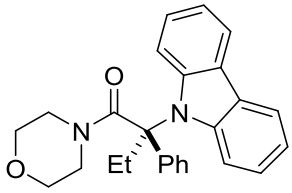
^{1}H NMR (500 MHz, d_6-DMSO, 80 °C) δ 8.12 (dd, *J* = 7.3, 1.6 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.30 (d, *J* = 6.8 Hz, 3H), 7.23 – 7.13 (m, 4H), 7.12 – 6.90 (m, 5H), 6.59 (s, 2H), 2.99 (s, 3H), 2.92 – 2.78 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, d_6-DMSO, 80 °C) δ 170.5, 144.4, 141.1, 140.5, 129.1, 128.8, 128.2, 128.1, 127.1, 126.8, 125.6, 124.2, 120.1, 119.7, 113.6, 73.8, 41.3, 32.2, 10.3;

FT-IR (ATR) 2936, 1651, 1593, 1473, 1445, 1367, 1315, 1213, 750, 723, 698 cm^{-1};

HRMS (FAB) *m/z* $(M)^{+\bullet}$ calcd for $C_{29}H_{26}N_2O$: 418.2045, found: 418.2048;

$[\alpha]^{25}_D$ (94% ee) = +10.0° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(Carbazol-9-yl)-1-morpholino-2-phenylbutan-1-one (Fig. 2B, Entry 10). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-1-morpholino-2-phenylbutan-1-one (160.7 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 30% Et_2O/hexanes). Colorless solid. First run: 145 mg (73% yield), 90% ee. Second run: 149 mg (75% yield), 90% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (3% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 15.4 min (minor), 22.9 min (major).

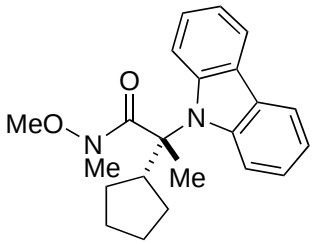
^{1}H NMR (500 MHz, d_6-DMSO, 80 °C) δ 8.20 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.47 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.30 (ddd, *J* = 8.6, 7.1, 1.4 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.37 – 3.22 (m, 4H), 3.09 – 2.84 (m, 6H), 0.66 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, d_6-DMSO, 80 °C) δ 168.9, 140.9, 139.9, 128.6, 128.3, 128.1, 125.9, 124.2, 120.5, 120.2, 113.9, 73.4, 65.6, 45.6, 32.0, 10.4;

FT-IR (ATR) 2923, 2855, 1635, 1592, 1475, 1417, 1315, 1269, 1228, 1112, 750, 717 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{26}H_{27}N_2O_2$: 399.2067, found: 399.2068;

$[\alpha]^{25}_D$ (90% ee) = +44.2° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*R*)-2-(Carbazol-9-yl)-2-cyclopentyl-*N*-methoxy-*N*-methylpropanamide (Fig. 2B, Entry 11). The title compound was synthesized according to General Procedure A from carbazole (83.6 mg, 0.50 mmol) and 2-chloro-2-cyclopentyl-*N*-methoxy-*N*-methylpropanamide (131.8 mg, 0.60 mmol). 5.0 mL of the stock solution of the catalyst were used (5.0 mol% CuCl). The product was purified by flash chromatography (0% →

7% Et_2O/hexanes). Sticky white solid. First run: 127 mg (73% yield), 95% ee. Second run: 127 mg (73% yield), 95% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 0.7 mL/min); retention times for compound obtained using (*S*)-**L***: 8.2 min (minor), 9.1 min (major).

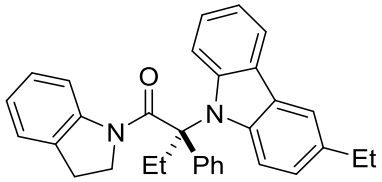
^{1}H NMR (500 MHz, d_6-DMSO, 80 °C) δ 8.22 – 8.08 (m, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.37 (ddd, *J* = 8.8, 7.2, 1.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 3.38 (dt, *J* = 10.6, 7.5 Hz, 1H), 2.97 (s, 3H), 2.52 (s, 3H), 2.27 (s, 3H), 2.14 – 2.00 (m, 1H), 1.60 – 1.52 (m, 3H), 1.43 (dt, *J* = 15.4, 5.6 Hz, 1H), 1.33 – 1.18 (m, 2H), 0.75 – 0.62 (m, 1H);

^{13}C NMR (126 MHz, d_6-DMSO, 80 °C) δ 173.5, 140.6, 126.1, 123.6, 120.3, 119.4, 112.7, 69.0, 59.4, 46.7, 33.9, 28.9, 27.2, 26.1, 24.4, 19.1.

FT-IR (ATR) 2939, 2865, 1644, 1592, 1473, 1445, 1372, 1317, 1223, 996, 741, 723 cm^{-1};

HRMS (ESI) *m/z* $(M)^+$ calcd for $C_{22}H_{26}N_2O_2$: 350.1994, found: 350.1987;

$[\alpha]^{25}_D$ (95% ee) = +172° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(3-Ethyl-carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 1). The title compound was synthesized according to General Procedure A from 3-ethylcarbazole (97.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 215 mg (94% yield), 93% ee. Second run: 219 mg (96% yield), 92% ee.

Gram-scale reaction: A solution of the catalyst was prepared by vigorously stirring CuCl (3.0 mg, 30 μmol) and (*S*)-**L*** (12.8 mg, 36 μmol) in toluene (7.2 mL) at 60 °C for 30 min under nitrogen. An oven-dried 250 mL round-bottom flask equipped with a stir bar was capped with a septum, cooled under vacuum, and then backfilled with nitrogen. 3-Ethylcarbazole (586 mg, 3.0 mmol) and Li*O*t*-Bu (360 mg, 4.5 mmol) were added to the flask, which was then placed under vacuum and refilled with nitrogen (three cycles). Then, toluene (100 mL) was added, and the mixture was stirred for 5 min. Next, the solution of catalyst was added, with the aid of toluene (0.8 mL), and the resulting mixture was stirred at r.t. for 20 min. 2-Chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (1.08 g, 3.6 mmol) was added to an oven-dried 20 mL vial, the vial was capped, and then it was evacuated and backfilled with nitrogen (three cycles). Toluene (12 mL) was added, and the solution was transferred via syringe to the reaction mixture. The mixture was degassed by applying three freeze-pump-thaw cycles. The reaction vial was backfilled with nitrogen and then detached from the Schlenk line, and the holes in the septum were covered by grease. The flask was placed ~5 cm from three 32 W blue LED lamps, and the reaction mixture was irradiated at −40 °C for 20 h under a nitrogen atmosphere. Next, the mixture was passed through a short plug of silica (eluent: Et_2O; monitored by

TLC). The resulting solution was concentrated under vacuum, and the residue was purified by flash chromatography (0% → 6% Et_2O/hexanes), which furnished 1.29 g (94% yield, 94% ee) of a colorless powder.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 7.1 min (minor), 9.1 min (major).

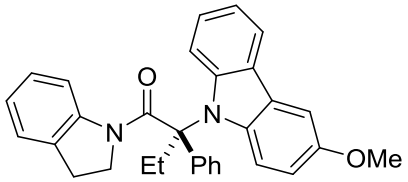
^{1}H NMR (500 MHz, d_6-DMSO, 80 °C) δ 8.24 (d, *J* = 8.2 Hz, 1H), 8.21 – 8.15 (m, 1H), 8.03 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.40 – 7.29 (m, 3H), 7.23 – 7.05 (m, 7H), 7.02 (td, *J* = 7.4, 1.1 Hz, 1H), 3.65 (ddd, *J* = 10.8, 9.3, 5.2 Hz, 1H), 3.17 – 3.10 (m, 1H), 3.07 – 2.98 (m, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.70 – 2.54 (m, 2H), 1.28 (t, *J* = 7.6 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, d_6-DMSO, 80 °C) δ 169.1, 144.2, 141.4, 139.6, 139.3, 135.7, 132.1, 128.8, 128.4, 128.2, 127.3, 126.2, 125.8, 124.9, 124.6, 124.3, 124.1, 120.5, 120.0, 119.2, 118.4, 113.3, 113.2, 74.0, 49.2, 31.8, 29.0, 28.2, 16.1, 10.5;

FT-IR (ATR) 2960, 1649, 1597, 1477, 1452, 1370, 1213, 875, 748, 717 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{32}H_{31}N_2O$: 459.2431, found: 459.2445;

$[\alpha]^{25}_D$ (93% ee) = –23.2° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-1-(Indolin-1-yl)-2-(3-methoxy-carbazol-9-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 2). The title compound was synthesized according to General Procedure A from 3-methoxy-carbazole (98.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 3.0 mL of the stock solution of the catalyst were used (3.0 mol% CuCl). The product was purified by flash chromatography (0% → 12% Et_2O/hexanes). Colorless solid. First run: 221 mg (96% yield), 90% ee. Second run: 204 mg (89% yield), 88% ee.

The ee was determined by HPLC on a Daicel CHIRALCEL® OD column (2% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 9.2 min (major), 12.4 min (minor).

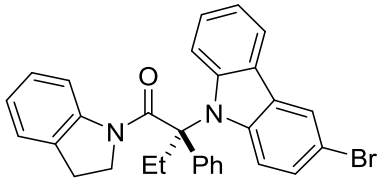
^{1}H NMR (500 MHz, d_6-DMSO, 80 °C) δ 8.24 (d, *J* = 8.2 Hz, 1H), 8.22 – 8.17 (m, 1H), 7.76 (d, *J* = 2.7 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.41 – 7.31 (m, 3H), 7.23 – 7.11 (m, 5H), 7.09 – 6.98 (m, 2H), 6.87 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.86 (s, 3H), 3.66 (ddd, *J* = 10.9, 9.4, 5.1 Hz, 1H), 3.13 (dt, *J* = 14.1, 7.2 Hz, 1H), 3.06 – 2.96 (m, 2H), 2.73 – 2.54 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, d_6-DMSO, 80 °C) δ 169.2, 154.2, 144.2, 141.7, 139.3, 135.9, 132.1, 128.8, 128.4, 128.2, 127.3, 126.0, 125.01, 124.95, 124.7, 124.1, 120.8, 119.7, 118.4, 114.8, 114.1, 113.3, 104.0, 74.0, 56.2, 49.2, 31.8, 29.0, 10.5;

FT-IR (ATR) 2935, 1674, 1597, 1477, 1455, 1374, 1320, 1291, 1200, 1173, 1032, 750, 717, 699 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{31}H_{29}N_2O_2$: 461.2224, found: 461.2225;

$[\alpha]^{25}_D$ (90% ee) = –22.0° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(3-Bromo-carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 3). The title compound was synthesized according to General Procedure A from 3-bromo-carbazole (123.1 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 3.0 mL of the stock solution of the catalyst were used (3.0 mol% CuCl). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 203 mg (80% yield), 93% ee. Second run: 210 mg (83% yield), 91% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 0.7 mL/min); retention times for compound obtained using (*S*)-**L***: 11.1 min (minor), 13.0 min (major).

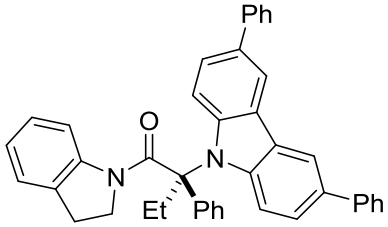
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.1 Hz, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 8.14 – 8.08 (m, 1H), 7.65 – 7.56 (m, 2H), 7.43 – 7.36 (m, 3H), 7.36 – 7.20 (m, 5H), 7.17 – 6.98 (m, 3H), 3.76 (ddd, *J* = 10.8, 9.2, 4.1 Hz, 1H), 3.27 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.15 (dt, *J* = 10.7, 9.2 Hz, 1H), 2.93 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.73 (dt, *J* = 15.4, 9.2 Hz, 1H), 2.64 (ddd, *J* = 15.5, 9.3, 4.1 Hz, 1H), 0.72 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 143.7, 141.5, 139.8, 137.4, 131.7, 128.7, 128.6, 128.1, 128.0, 127.4, 126.3, 126.1, 124.7, 124.4, 123.1, 122.7, 120.3, 120.2, 120.0, 119.9, 118.9, 112.9, 74.2, 49.2, 32.2, 29.3, 10.3;

FT-IR (ATR) 2935, 1648, 1597, 1476, 1441, 1262, 1213, 1030, 868, 722, 700 cm^{-1};

HRMS (ESI) *m/z* $(M)^+$ calcd for $C_{30}H_{25}{}^{81}BrN_2O$: 510.1130, found: 510.1136;

$[\alpha]^{25}_D$ (93% ee) = –17.7° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(3,6-Diphenyl-carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 4). The title compound was synthesized according to General Procedure A from 3,6-diphenyl-carbazole (159.7 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). The product was purified by flash chromatography (0% → 10% Et_2O/hexanes). Colorless solid. First run: 286 mg (98% yield), 91% ee. Second run: 288 mg (99% yield), 88% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 10.5 min (major), 11.7 min (minor).

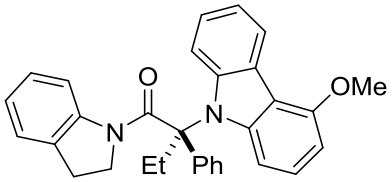
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.45 (m, 3H), 7.82 – 7.75 (m, 4H), 7.73 – 7.68 (m, 2H), 7.59 – 7.49 (m, 6H), 7.49 – 7.38 (m, 5H), 7.38 – 7.19 (m, 3H), 7.19 – 7.09 (m, 2H), 3.91 (ddd, *J* = 10.8, 9.3, 4.0 Hz, 1H), 3.35 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.26 (dt, *J* = 10.7, 9.2 Hz, 1H), 3.04 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.68 (ddd, *J* = 15.5, 9.3, 4.0 Hz, 1H), 0.83 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 143.9, 141.3, 141.1, 137.7, 133.3, 131.8, 128.9, 128.8, 128.04, 127.99, 127.4, 127.2, 126.8, 125.1, 125.0, 124.6, 124.5, 119.0, 118.3, 113.8, 74.2, 49.3, 32.4, 29.3, 10.5;

FT-IR (ATR) 2935, 1651, 1598, 1474, 1457, 1374, 1264, 1216, 1078, 878, 756, 695 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{42}H_{35}N_2O$: 583.2744, found: 583.2748;

$[\alpha]^{25}_D$ (91% ee) = –20.8° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-1-(indolin-1-yl)-2-(4-methoxy-carbazol-9-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 5). The title compound was synthesized according to General Procedure A from 4-methoxy-carbazole (98.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 3.0 mL of the stock solution of the catalyst were used (3.0 mol% CuCl). The product was purified by flash chromatography (0% → 10% Et_2O/hexanes). Colorless solid. First run: 196 mg (85% yield), 93% ee. Second run: 206 mg (89% yield), 92% ee.

The ee was determined by HPLC on a Daicel CHIRALCEL® OD column (1% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 6.8 min (major), 9.0 min (minor).

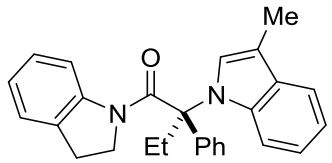
^{1}H NMR (500 MHz, d_6-DMSO, 100 °C) δ 8.42 – 8.32 (m, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.23 – 7.14 (m, 5H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.81 (dd, *J* = 10.8, 8.2 Hz, 2H), 4.07 (d, *J* = 1.3 Hz, 3H), 3.63 (td, *J* = 10.0, 5.2 Hz, 1H), 3.23 – 3.01 (m, 3H), 2.62 (dtd, *J* = 25.4, 15.7, 15.3, 7.1 Hz, 2H), 0.77 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, d_6-DMSO, 100 °C) δ 169.2, 156.4, 144.2, 142.6, 140.5, 139.4, 132.1, 128.8, 128.3, 128.2, 127.3, 126.7, 124.90, 124.88, 124.6, 123.5, 123.3, 120.2, 118.4, 113.3, 113.0, 106.4, 102.1, 74.3, 56.0, 49.2, 31.9, 29.0, 10.5;

FT-IR (ATR) 2932, 1648, 1595, 1476, 1434, 1374, 1258, 1113, 1027, 749, 718 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{31}H_{29}N_2O_2$: 461.2224, found: 461.2225;

$[\alpha]^{25}_D$ (93% ee) = –27.6° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-1-(Indolin-1-yl)-2-(3-methyl-indol-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 6). The title compound was synthesized according to General Procedure A from 3-methyl-indole (65.5 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 5.0 mL of the stock solution of the catalyst were used (5.0 mol% CuCl). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 155 mg (79% yield), 92% ee. Second run: 156 mg (79% yield), 92% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® AD column (1% *i*-PrOH/hexanes, 0.7 mL/min); retention times for compound obtained using (*S*)-**L***: 8.9 min (minor), 10.0 min (major).

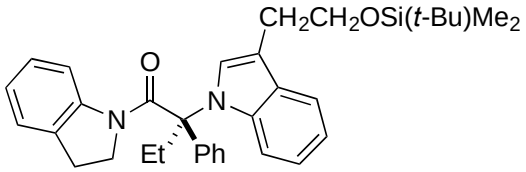
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.61 (ddd, *J* = 7.7, 1.6, 0.7 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.48 – 7.37 (m, 3H), 7.35 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.28 (tdd, *J* = 8.2, 1.5, 0.8 Hz, 1H), 7.21 (q, *J* = 1.1 Hz, 1H), 7.17 – 7.10 (m, 3H), 7.10 – 7.05 (m, 1H), 3.27 – 3.14 (m, 2H), 2.97 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.84 – 2.76 (m, 2H), 2.66 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.38 (d, *J* = 1.1 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 143.9, 137.5, 136.2, 131.4, 130.0, 128.6, 128.3, 128.0, 127.4, 124.7, 124.4, 124.3, 122.0, 119.4, 119.1, 118.4, 112.9, 111.0, 73.1, 48.4, 33.4, 28.8, 9.9, 9.8;

FT-IR (ATR) 2933, 1651, 1598, 1477, 1455, 1381, 1262, 1182, 1019, 739, 702 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{27}H_{27}N_2O$: 395.2118, found: 395.2120;

$[\alpha]^{25}_D$ (92% ee) = –17.9° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(3-(2-((*Tert*-butyldimethylsilyl)oxy)ethyl)-indol-1-yl)-1-(indolin-1-yl)-2-phenyl-butan-1-one (Fig. 2C, Entry 7). The title compound was synthesized according to General Procedure A from 3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-indole (*34*) (137.7 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 5.0 mL of the stock solution of the catalyst were used (5.0 mol% CuCl). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 215 mg (80% yield), 92% ee. Second run: 214 mg (79% yield), 92% ee.

The ee was determined by HPLC on a Daicel CHIRALPAK® IB column (0.5% *i*-PrOH/hexanes, 0.7 mL/min); retention times for compound obtained using (*S*)-**L***: 8.0 min (minor), 8.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.2 Hz, 1H), 7.65 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.49 – 7.34 (m, 4H), 7.33 – 7.25 (m, 2H), 7.18 – 7.04 (m, 4H), 3.93

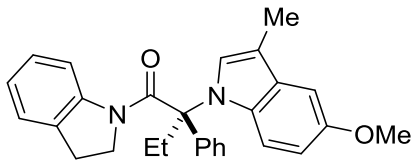
(dd, *J* = 7.5, 6.1 Hz, 2H), 3.29 – 3.09 (m, 2H), 3.07 – 2.93 (m, 3H), 2.79 (t, *J* = 8.1 Hz, 2H), 2.65 (dq, *J* = 14.3, 7.2 Hz, 1H), 0.93 (d, *J* = 1.1 Hz, 9H), 0.79 (td, *J* = 7.2, 1.1 Hz, 3H), 0.09 (d, *J* = 1.1 Hz, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 143.8, 137.4, 136.1, 131.4, 129.5, 128.6, 128.3, 128.0, 127.4, 125.1, 124.3, 124.3, 122.0, 119.5, 119.2, 118.5, 113.0, 112.7, 73.1, 63.7, 48.4, 33.4, 28.9, 28.8, 26.0, 18.3, 10.0, –5.2, –5.3;

FT-IR (ATR) 2927, 2854, 1653, 1600, 1478, 1456, 1387, 1256, 1180, 1073, 831, 757 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{34}H_{43}N_2O_2Si$: 539.3088, found: 539.3091;

$[\alpha]^{25}_D$ (92% ee) = –4.1° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-1-(Indolin-1-yl)-2-(5-methoxy-3-methyl-indol-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 8). The title compound was synthesized according to General Procedure A from 5-methoxy-3-methyl-indole (*35*) (74.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 5.0 mL of the stock solution of the catalyst were used (5.0 mol% CuCl). The product was purified by flash chromatography (0% → 11% Et_2O/hexanes). Colorless solid. First run: 182 mg (86% yield), 88% ee. Second run: 184 mg (87% yield), 88% ee.

The ee was determined by HPLC on a Daicel CHIRALCEL® OD column (2% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 6.8 min (minor), 7.7 min (major).

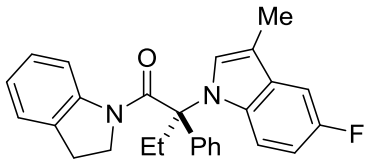
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.35 (m, 3H), 7.28 (dddd, *J* = 8.2, 6.6, 1.6, 0.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.18 (d, *J* = 1.3 Hz, 1H), 7.14 (ddt, *J* = 6.5, 1.6, 0.7 Hz, 1H), 7.07 (td, *J* = 7.4, 1.1 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.76 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.89 (s, 3H), 3.23 (q, *J* = 8.2 Hz, 2H), 2.91 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.81 (td, *J* = 8.0, 3.1 Hz, 2H), 2.65 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.34 (d, *J* = 1.0 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 153.9, 143.9, 137.7, 131.41, 131.38, 130.5, 128.5, 128.3, 128.0, 127.4, 125.4, 124.4, 124.3, 118.4, 113.7, 111.8, 110.5, 100.8, 73.1, 55.7, 48.4, 33.5, 28.8, 9.89, 9.87;

FT-IR (ATR) 2934, 1661, 1598, 1477, 1456, 1376, 1262, 1241, 1218, 1078, 1060, 754 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{28}H_{29}N_2O_2$: 425.2222, found: 425.2224;

$[\alpha]^{25}_D$ (88% ee) = –15.5° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).



(*S*)-2-(5-Fluoro-3-methyl-indol-1-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 9). The title compound was synthesized according to General Procedure A from 5-fluoro-3-methyl-indole (74.6 mg, 0.50 mmol) and 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (179.9 mg, 0.60 mmol). 5.0 mL of the stock solution of the catalyst were used (5.0 mol% CuCl). The product was purified by flash chromatography (0% → 7% Et_2O/hexanes). Colorless solid. First run: 201 mg (98% yield), 94% ee. Second run: 201 mg (97% yield), 94% ee.

X-ray quality crystals were obtained by slow diffusion of pentane into a saturated solution in benzene of a sample synthesized with (*S*)-**L***.

The ee was determined by HPLC on a Daicel CHIRALCEL® OD column (2% *i*-PrOH/hexanes, 1.0 mL/min); retention times for compound obtained using (*S*)-**L***: 7.1 min (minor), 8.6 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.39 (m, 1H), 7.56 – 7.48 (m, 2H), 7.48 – 7.36 (m, 3H), 7.29 – 7.21 (m, 4H), 7.15 (ddq, *J* = 7.4, 1.7, 1.0 Hz, 1H), 7.08 (td, *J* = 7.4, 1.1 Hz, 1H), 6.85 (td, *J* = 9.1, 2.6 Hz, 1H), 3.20 (q, *J* = 7.7 Hz, 2H), 2.93 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.84 – 2.77 (m, 2H), 2.64 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.34 (d, *J* = 1.1 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 157.7 (d, *J* = 235.8 Hz), 143.8, 137.4, 132.7, 131.3, 130.5 (d, *J* = 9.3 Hz), 128.5, 128.4, 128.1, 127.4, 126.3, 124.43, 124.41, 118.4, 113.5 (d, *J* = 9.2 Hz), 111.0 (d, *J* = 4.7 Hz), 110.4 (d, *J* = 25.8 Hz), 104.0 (d, *J* = 22.9 Hz), 73.1, 48.4, 33.4, 28.8, 9.9, 9.8;

FT-IR (ATR) 2935, 1650, 1598, 1454, 1377, 1263, 1190, 917, 849, 754, 699 cm^{-1};

HRMS (ESI) *m/z* $(M+H)^+$ calcd for $C_{27}H_{26}FN_2O$: 413.2024, found: 413.2023;

$[\alpha]^{25}_D$ (94% ee) = –14.3° (c = 0.50, $CHCl_3$, obtained with (*S*)-**L***).

Fig. 3A. In a nitrogen-filled glovebox, a stock solution of the catalyst was prepared by vigorously stirring CuCl (1.0 mg, 0.010 mmol) and (*S*)-**L*** (4.3 mg, 0.012 mmol) in toluene (2.0 mL) for 30 min, with warming by a heat gun. Carbazole (8.4 mg, 0.050 mmol), LiO*t*-Bu (6.0 mg, 0.075 mmol), a stir bar, and toluene (1.4 mL) were added to a 4 mL vial. The resulting mixture was stirred for 5 min, and then the stock solution of the catalyst (100 μL) was added, and stirring was continued for 20 min. Enantiopure electrophile ((+)- or (−)-2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one; >99% ee; 500 μL aliquot of a 0.12 M stock solution; 18.0 mg, 0.060 mmol) was added, then the vial was sealed with a PTFE-lined septum cap, taken out of the glovebox, placed ~5 cm from two 32 W blue LED lamps, and irradiated at −40 °C for 16 h under a nitrogen atmosphere. Next, the mixture was allowed to warm to r.t., and dibenzyl ether (19 μL; 0.10 mmol) was added as an internal standard. A portion (~1 mL) of the reaction mixture was passed through a short plug of silica to remove traces of copper. The yield of the product was determined by ^{1}H NMR analysis using dibenzyl ether as an internal standard. After purification by preparative TLC (17% EtOAc/hexanes), the ee of the unreacted

electrophile and the product were determined by HPLC on a Daicel CHIRALPAK® AD column (3% *i*-PrOH/hexanes, 1.0 mL/min).

Reaction starting with (+)-2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one: Product shown in Fig. 2B, Entry 1 was synthesized in 95% yield and 94% ee. Unreacted electrophile was found to have 98% ee.

Unreacted electrophile retention times: 6.2 min (minor), 7.9 min (major);

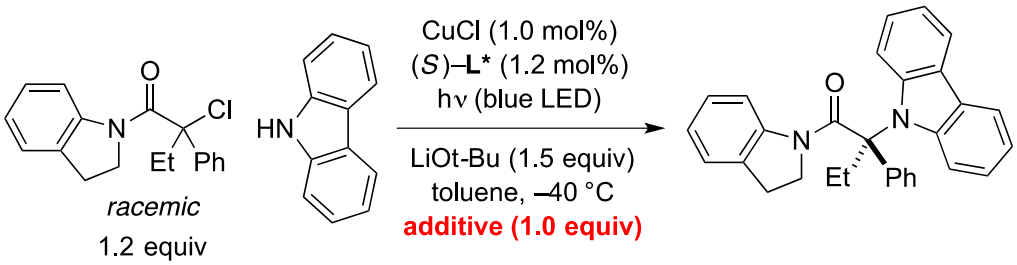
Product retention times: 6.3 min (minor), 7.8 min (major).

Reaction starting with (−)-2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one: Product shown in Fig. 2B, Entry 1 was synthesized in 96% yield and 93% ee. Unreacted electrophile was found to have 98% ee.

Unreacted electrophile retention times: 6.2 min (major), 7.9 min (minor);

Product retention times: 6.3 min (minor), 7.8 min (major).

IV. Additive and Ligand Effects



In a nitrogen-filled glovebox, a stock solution of the catalyst was prepared by vigorously stirring CuCl (1.0 mg, 0.010 mmol) and (*S*)-**L*** (4.3 mg, 0.012 mmol) in toluene (2.0 mL) for 30 min, with warming by a heat gun. Carbazole (16.7 mg, 0.10 mmol), LiO*t*-Bu (12.0 mg, 0.15 mmol), a stir bar, and toluene (2.8 mL) were added to a 4 mL vial. The resulting mixture was stirred for 5 min, and then the stock solution of the catalyst (200 µL) was added, and stirring was continued for 20 min. 2-Chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (1.0 mL aliquot of a 0.12 M stock solution; 36.0 mg, 0.12 mmol) and then the additive (0.10 mmol) were added to the reaction mixture, and then the vial was sealed with a PTFE-lined septum cap, taken out of the glovebox, placed ~5 cm from two 32 W blue LED lamps, and irradiated at −40 °C for 16 h under a nitrogen atmosphere. Next, the mixture was allowed to warm to r.t., and dibenzyl ether (19 µL; 0.10 mmol) was added as an internal standard. A portion (~ 1.5 mL) of the reaction mixture was passed through a short plug of silica to remove traces of copper. The recovery of the additive was determined by GC analysis, and the yield of the product was determined by ^{1}H NMR analysis, both using dibenzyl ether as an internal standard. After purification by preparative TLC (17% EtOAc/hexanes), the ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times: 6.2 min (minor), 7.7 min (major).

Table S1–A. Effect of additives (1.0 equiv) on cross-couplings (average of two experiments).

entry	additive	yield (%)	ee (%)	recovered additive (%)
1	cyclohexyl bromide	95	94	90
2	2-nonanone	92	94	96
3	5-nonanol	90	94	99
4	methyl octanoate	92	94	98
5	*cis*-5-decene	96	95	>99
6	*trans*-5-decene	98	95	>99
7	5-decyne	97	94	>99
8	valeronitrile	94	94	80
9	3-phenylpropylamine	7	28	87
10	*N*-methyl-2-phenylethylamine	12	86	89
11	*n*-octanal	40	90	4

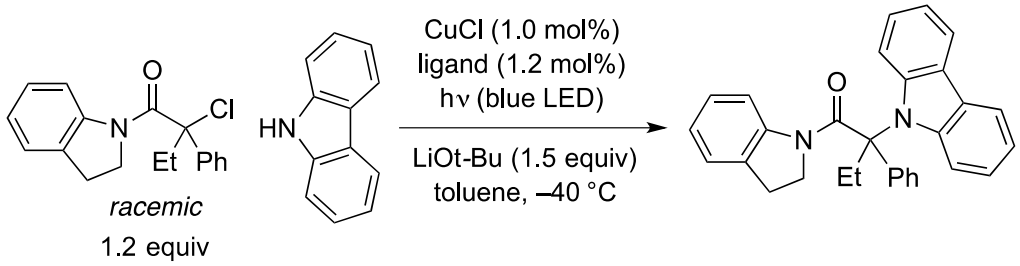
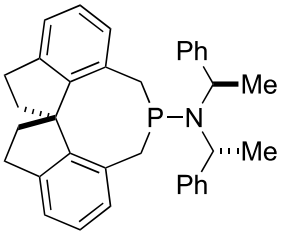
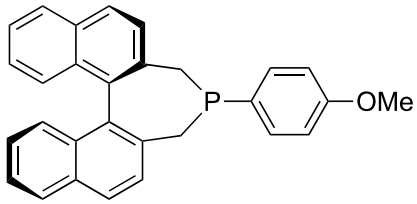


Table S1–L. Effect of ligands on cross-couplings (average of two experiments).

entry	ligand	yield (%)
1	1,10-phenanthroline	6
2	neocuproine	12
3	bpy	2
4	TMEDA	8
5	**L1**	20
6	**L2**	63

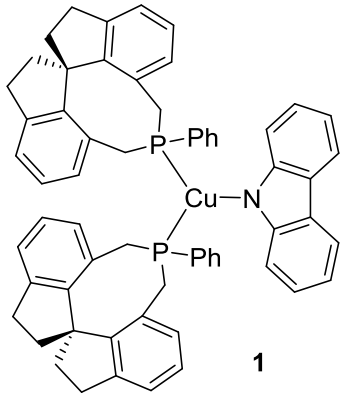


L1



L2

V. Synthesis and Reactivity of Copper–Carbazolide Complex 1



1

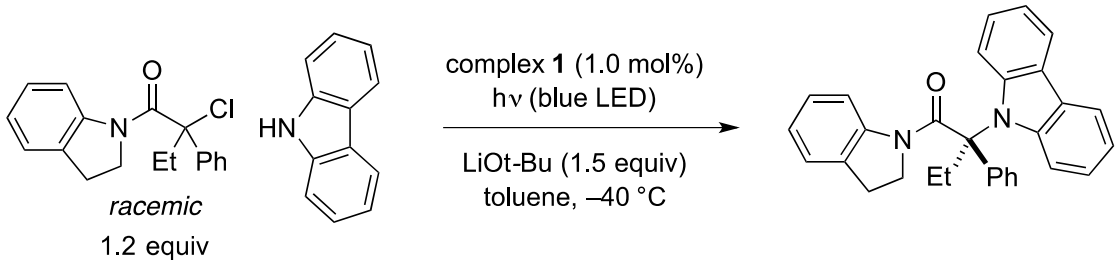
Preparation of complex 1. In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with carbazole (16.7 mg, 0.10 mmol), a stir bar, and a solution of mesitylcopper (18.2 mg, 0.10 mmol) in benzene (400 μL). The mixture was stirred for 10 min, and then a solution of (*R*)-**L*** (70.8 mg, 0.20 mmol) in benzene (600 μL) was added. The resulting reaction mixture was stirred for 6 h, and then pentane (2.0 mL) was added dropwise. This mixture was stirred for 1 h, during which time a white precipitate formed. The white precipitate was filtered, rinsed with pentane (5 mL), and dried to give 64 mg (64% yield) of the desired product as a white powder.

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in a mixture of benzene/ether/pentane.

^{1}H NMR (400 MHz, C_6D_6) δ 8.74 – 8.41 (m, 2H), 7.41 (p, *J* = 6.6 Hz, 4H), 7.11 (t, *J* = 7.5 Hz, 4H), 7.01 – 6.80 (m, 10H), 6.74 (d, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 2H), 5.65 (d, *J* = 7.7 Hz, 2H), 3.56 (d, *J* = 14.3 Hz, 2H), 3.27 (s, 2H), 2.91 – 2.53 (m, 12H), 2.16 – 1.78 (m, 8H), 1.30 – 1.15 (m, 2H), 0.95 (t, *J* = 6.9 Hz, 2H);

^{13}C NMR (101 MHz, C_6D_6) δ 151.0, 147.6, 147.0, 143.1, 142.5, 132.3, 129.8, 129.6, 129.5, 128.8, 128.6, 128.3, 126.2, 125.6, 123.5, 123.2, 123.1, 120.2, 115.0, 114.4, 61.4, 38.3, 37.6, 30.6, 30.4, 30.1, 25.0;

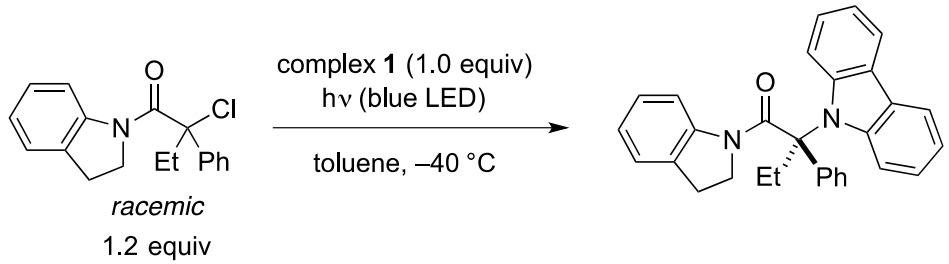
^{31}P NMR (162 MHz, C_6D_6) δ –13.9.



Use of complex 1 as a catalyst. In a nitrogen-filled glovebox, a stock solution of catalyst was prepared by vigorously stirring complex **1** (1.9 mg, 2.0 μmol) in toluene (400 μL) for 30 min. Carbazole (16.7 mg, 0.10 mmol) and LiO*t*-Bu (12.0 mg, 0.15 mmol) were added to a 4 mL vial, followed by a stir bar and toluene (2.8 mL). The mixture was stirred for 5 min, and then the stock solution of complex **1** (200 μL) was

added, and the resulting mixture was stirred for 20 min. 2-Chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (1.0 mL aliquot of a 0.12 M solution in toluene; 36.0 mg, 0.12 mmol) was added to the reaction mixture, and then the vial was sealed with a PTFE-lined septum cap and taken out of the glovebox. The vial was placed ~5 cm from two 32 W blue LED lamps, and the reaction mixture was irradiated at −40 °C for 16 h under a nitrogen atmosphere. Dibenzyl ether (19 μL, 0.10 mmol) was added as an internal standard, and the yield was determined through analysis by ^{1}H NMR spectroscopy. (*R*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one was produced in 92% yield and 94% ee.

After purification by preparative TLC (17% EtOAc/hexanes), the ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times: 6.2 min (major), 7.7 min (minor).



Stoichiometric reaction of complex 1 in the stoichiometric reaction. In a nitrogen-filled glovebox, complex **1** (23.5 mg, 0.025 mmol), a stir bar, and toluene (3.0 mL) were added in turn to a 4 mL vial. The mixture was stirred for 5 min, and then 2-chloro-1-(indolin-1-yl)-2-phenylbutan-1-one (1.0 mL aliquot of a 0.030 M solution in toluene; 9.0 mg, 0.030 mmol) was added. The vial was sealed with a PTFE-lined septum cap and then taken out of the glovebox. The vial was placed ~5 cm from two 32 W blue LED lamps, and the reaction mixture was irradiated at −40 °C for 16 h under a nitrogen atmosphere. Dibenzyl ether (19 μL, 0.10 mmol) was added as an internal standard, and the yield was determined through analysis by ^{1}H NMR spectroscopy. (*R*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one was produced in 72% yield and 92% ee.

After purification by preparative TLC (17% EtOAc/hexanes), the ee was determined by HPLC on a Daicel CHIRALPAK® AD column (5% *i*-PrOH/hexanes, 1.0 mL/min); retention times: 6.2 min (major), 7.7 min (minor).

VI. X-Ray Crystallography/Determination of Absolute Stereochemistry

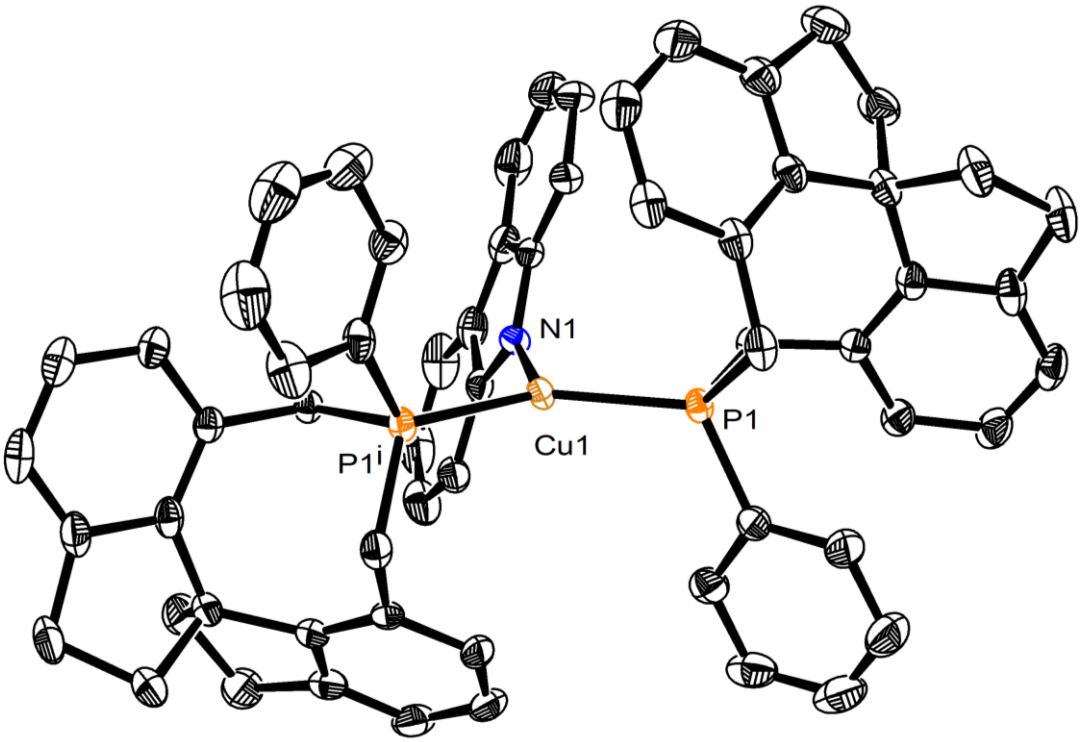


Fig. S2. Complex **1**; structure determined by X-ray diffraction. Ellipsoids are shown at 50% probability level, and H atoms have been omitted for clarity.

Complex 1. X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution of a sample in a mixture of benzene/ether/pentane. A crystal of $C_{62}H_{54}CuNP_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon CMOS diffractometer with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2 (*36*), the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package (*37*) using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S2. Crystal data and structure refinement for p15103.

Identification code	p15103	
Empirical formula	$C_{62}H_{54}CuNP_2$	
Formula weight	938.54	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P6_4$	
Unit cell dimensions	a = 16.9595(8) Å	α = 90°.
	b = 16.9595(8) Å	β = 90 °.
	c = 14.4217(7) Å	γ = 120 °.
Volume	3592.3(4) $Å^3$	
Z	3	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	0.565 mm^{-1}	
F(000)	1476	
Crystal size	0.16 x 0.05 x 0.03 mm^3	
Theta range for data collection	2.402 to 37.529°.	
Index ranges	-28<=h<=28, -28<=k<=27, -23<=l<=24	
Reflections collected	102576	
Independent reflections	12026 [R(int) = 0.1009]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9012	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12026 / 1 / 299	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0659, wR2 = 0.1093	
R indices (all data)	R1 = 0.1484, wR2 = 0.1283	
Absolute structure parameter	0.022(4)	
Largest diff. peak and hole	1.015 and -0.377 $e/Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for p15103. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	10000	4144(1)	20(1)
P(1)	3642(1)	8942(1)	3600(1)	19(1)
N(1)	5000	10000	5522(2)	20(1)
C(1)	5452(2)	9711(2)	6091(2)	22(1)
C(2)	6008(2)	9353(2)	5840(3)	29(1)
C(3)	6399(3)	9103(3)	6537(3)	42(1)
C(4)	6247(3)	9199(3)	7476(4)	53(1)
C(5)	5697(3)	9545(3)	7733(3)	44(1)
C(6)	5295(2)	9812(2)	7047(2)	29(1)
C(7)	2863(2)	8513(2)	4613(2)	18(1)
C(8)	1275(2)	8004(2)	4017(2)	23(1)
C(9)	1922(2)	7794(2)	4356(2)	20(1)
C(10)	1700(2)	6881(2)	4380(2)	27(1)
C(11)	859(2)	6189(2)	4064(3)	34(1)
C(12)	228(2)	6400(2)	3713(2)	34(1)
C(13)	435(2)	7310(2)	3685(2)	30(1)
C(14)	-132(2)	7691(3)	3328(3)	41(1)
C(15)	575(2)	8710(3)	3213(3)	37(1)
C(16)	1292(2)	8911(2)	3978(2)	25(1)
C(17)	969(2)	9113(3)	4911(3)	35(1)
C(18)	1268(3)	10128(3)	4870(3)	41(1)
C(19)	2104(2)	10512(2)	4266(3)	30(1)
C(20)	2773(3)	11413(3)	4146(3)	36(1)
C(21)	3513(3)	11611(2)	3583(3)	35(1)
C(22)	3585(2)	10927(2)	3158(2)	28(1)
C(23)	2903(2)	10014(2)	3241(2)	23(1)
C(24)	2155(2)	9816(2)	3802(2)	25(1)
C(25)	3021(2)	9275(2)	2791(2)	24(1)
C(26)	3522(2)	7886(2)	3135(2)	26(1)
C(27)	2845(3)	7339(3)	2493(3)	38(1)
C(28)	2720(3)	6491(3)	2252(3)	51(1)
C(29)	3268(3)	6187(3)	2624(3)	50(1)
C(30)	3951(3)	6727(3)	3241(3)	41(1)
C(31)	4078(2)	7583(2)	3489(2)	30(1)

Table S4. Bond lengths [Å] and angles [°] for p15103.

Cu(1)-P(1)#1	2.2381(8)
Cu(1)-P(1)	2.2381(8)
Cu(1)-N(1)	1.988(4)
P(1)-C(7)	1.856(3)
P(1)-C(25)	1.840(3)
P(1)-C(26)	1.826(3)
N(1)-C(1)	1.369(4)
N(1)-C(1)#1	1.369(4)
C(1)-C(2)	1.402(4)
C(1)-C(6)	1.430(5)
C(2)-H(2)	0.9500
C(2)-C(3)	1.382(5)
C(3)-H(3)	0.9500
C(3)-C(4)	1.404(7)
C(4)-H(4)	0.9500
C(4)-C(5)	1.377(7)
C(5)-H(5)	0.9500
C(5)-C(6)	1.401(5)
C(6)-C(6)#1	1.429(8)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(7)-C(9)	1.493(4)
C(8)-C(9)	1.399(4)
C(8)-C(13)	1.403(4)
C(8)-C(16)	1.526(5)
C(9)-C(10)	1.399(4)
C(10)-H(10)	0.9500
C(10)-C(11)	1.395(5)
C(11)-H(11)	0.9500
C(11)-C(12)	1.384(6)
C(12)-H(12)	0.9500
C(12)-C(13)	1.401(5)
C(13)-C(14)	1.492(5)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(15)	1.543(5)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(16)	1.548(5)
C(16)-C(17)	1.555(5)
C(16)-C(24)	1.522(4)

C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(17)-C(18)	1.533(5)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(18)-C(19)	1.508(5)
C(19)-C(20)	1.386(5)
C(19)-C(24)	1.396(5)
C(20)-H(20)	0.9500
C(20)-C(21)	1.388(6)
C(21)-H(21)	0.9500
C(21)-C(22)	1.369(5)
C(22)-H(22)	0.9500
C(22)-C(23)	1.401(4)
C(23)-C(24)	1.397(5)
C(23)-C(25)	1.510(5)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.404(5)
C(26)-C(31)	1.377(5)
C(27)-H(27)	0.9500
C(27)-C(28)	1.389(6)
C(28)-H(28)	0.9500
C(28)-C(29)	1.376(7)
C(29)-H(29)	0.9500
C(29)-C(30)	1.384(7)
C(30)-H(30)	0.9500
C(30)-C(31)	1.403(5)
C(31)-H(31)	0.9500

P(1)#1-Cu(1)-P(1)	138.98(5)
N(1)-Cu(1)-P(1)#1	110.51(2)
N(1)-Cu(1)-P(1)	110.51(2)
C(7)-P(1)-Cu(1)	106.48(10)
C(25)-P(1)-Cu(1)	119.59(11)
C(25)-P(1)-C(7)	102.47(14)
C(26)-P(1)-Cu(1)	118.66(11)
C(26)-P(1)-C(7)	101.32(14)
C(26)-P(1)-C(25)	105.58(16)
C(1)#1-N(1)-Cu(1)	126.82(18)
C(1)-N(1)-Cu(1)	126.82(18)
C(1)-N(1)-C(1)#1	106.4(4)
N(1)-C(1)-C(2)	128.2(3)

N(1)-C(1)-C(6)	111.3(3)
C(2)-C(1)-C(6)	120.5(3)
C(1)-C(2)-H(2)	120.8
C(3)-C(2)-C(1)	118.4(4)
C(3)-C(2)-H(2)	120.8
C(2)-C(3)-H(3)	119.3
C(2)-C(3)-C(4)	121.4(4)
C(4)-C(3)-H(3)	119.3
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-C(3)	120.8(4)
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-H(5)	120.3
C(4)-C(5)-C(6)	119.4(4)
C(6)-C(5)-H(5)	120.3
C(5)-C(6)-C(1)	119.5(4)
C(5)-C(6)-C(6)#1	135.0(3)
C(6)#1-C(6)-C(1)	105.49(19)
P(1)-C(7)-H(7A)	109.1
P(1)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
C(9)-C(7)-P(1)	112.7(2)
C(9)-C(7)-H(7A)	109.1
C(9)-C(7)-H(7B)	109.1
C(9)-C(8)-C(13)	120.2(3)
C(9)-C(8)-C(16)	130.4(3)
C(13)-C(8)-C(16)	109.4(3)
C(8)-C(9)-C(7)	122.2(3)
C(10)-C(9)-C(7)	118.9(3)
C(10)-C(9)-C(8)	118.6(3)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-C(9)	121.3(3)
C(11)-C(10)-H(10)	119.3
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-C(10)	119.9(3)
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-H(12)	120.1
C(11)-C(12)-C(13)	119.7(3)
C(13)-C(12)-H(12)	120.1
C(8)-C(13)-C(14)	111.0(3)
C(12)-C(13)-C(8)	120.3(3)
C(12)-C(13)-C(14)	128.7(3)
C(13)-C(14)-H(14A)	111.3
C(13)-C(14)-H(14B)	111.3

C(13)-C(14)-C(15)	102.4(3)
H(14A)-C(14)-H(14B)	109.2
C(15)-C(14)-H(14A)	111.3
C(15)-C(14)-H(14B)	111.3
C(14)-C(15)-H(15A)	110.8
C(14)-C(15)-H(15B)	110.8
C(14)-C(15)-C(16)	104.8(3)
H(15A)-C(15)-H(15B)	108.9
C(16)-C(15)-H(15A)	110.8
C(16)-C(15)-H(15B)	110.8
C(8)-C(16)-C(15)	100.8(3)
C(8)-C(16)-C(17)	111.1(3)
C(15)-C(16)-C(17)	109.9(3)
C(24)-C(16)-C(8)	123.1(3)
C(24)-C(16)-C(15)	110.9(3)
C(24)-C(16)-C(17)	100.9(3)
C(16)-C(17)-H(17A)	110.7
C(16)-C(17)-H(17B)	110.7
H(17A)-C(17)-H(17B)	108.8
C(18)-C(17)-C(16)	105.0(3)
C(18)-C(17)-H(17A)	110.7
C(18)-C(17)-H(17B)	110.7
C(17)-C(18)-H(18A)	111.2
C(17)-C(18)-H(18B)	111.2
H(18A)-C(18)-H(18B)	109.2
C(19)-C(18)-C(17)	102.6(3)
C(19)-C(18)-H(18A)	111.2
C(19)-C(18)-H(18B)	111.2
C(20)-C(19)-C(18)	128.5(4)
C(20)-C(19)-C(24)	120.7(3)
C(24)-C(19)-C(18)	110.8(3)
C(19)-C(20)-H(20)	120.6
C(19)-C(20)-C(21)	118.8(4)
C(21)-C(20)-H(20)	120.6
C(20)-C(21)-H(21)	119.7
C(22)-C(21)-C(20)	120.6(3)
C(22)-C(21)-H(21)	119.7
C(21)-C(22)-H(22)	119.2
C(21)-C(22)-C(23)	121.6(3)
C(23)-C(22)-H(22)	119.2
C(22)-C(23)-C(25)	120.1(3)
C(24)-C(23)-C(22)	117.7(3)
C(24)-C(23)-C(25)	122.1(3)

C(19)-C(24)-C(16)	109.8(3)
C(19)-C(24)-C(23)	120.4(3)
C(23)-C(24)-C(16)	129.7(3)
P(1)-C(25)-H(25A)	110.0
P(1)-C(25)-H(25B)	110.0
C(23)-C(25)-P(1)	108.4(2)
C(23)-C(25)-H(25A)	110.0
C(23)-C(25)-H(25B)	110.0
H(25A)-C(25)-H(25B)	108.4
C(27)-C(26)-P(1)	122.9(3)
C(31)-C(26)-P(1)	118.0(3)
C(31)-C(26)-C(27)	119.0(3)
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-C(26)	120.0(4)
C(28)-C(27)-H(27)	120.0
C(27)-C(28)-H(28)	119.7
C(29)-C(28)-C(27)	120.5(4)
C(29)-C(28)-H(28)	119.7
C(28)-C(29)-H(29)	120.0
C(28)-C(29)-C(30)	120.0(4)
C(30)-C(29)-H(29)	120.0
C(29)-C(30)-H(30)	120.2
C(29)-C(30)-C(31)	119.7(4)
C(31)-C(30)-H(30)	120.2
C(26)-C(31)-C(30)	120.7(4)
C(26)-C(31)-H(31)	119.6
C(30)-C(31)-H(31)	119.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,z

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for p15103. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	13(1)	22(1)	22(1)	0	0	8(1)
P(1)	15(1)	22(1)	17(1)	1(1)	1(1)	7(1)
N(1)	19(2)	21(2)	22(2)	0	0	12(1)
C(1)	18(1)	17(1)	26(2)	2(1)	-2(1)	6(1)
C(2)	22(1)	22(1)	42(2)	4(1)	-1(1)	11(1)
C(3)	31(2)	32(2)	67(3)	14(2)	-6(2)	18(2)
C(4)	35(2)	45(2)	66(3)	29(2)	-14(2)	11(2)
C(5)	39(2)	48(2)	27(2)	13(2)	-5(2)	7(2)
C(6)	26(2)	27(2)	24(2)	4(1)	-2(1)	5(1)
C(7)	18(1)	20(1)	14(1)	1(1)	1(1)	7(1)
C(8)	17(1)	26(2)	18(1)	1(1)	5(1)	5(1)
C(9)	20(1)	22(1)	15(1)	2(1)	4(1)	8(1)
C(10)	23(2)	23(2)	28(2)	3(1)	6(1)	7(1)
C(11)	29(2)	22(2)	38(2)	-1(2)	7(2)	4(1)
C(12)	23(2)	27(2)	32(2)	-4(1)	4(1)	-2(1)
C(13)	18(1)	33(2)	28(2)	4(1)	1(1)	4(1)
C(14)	16(2)	42(2)	51(2)	7(2)	-4(2)	4(2)
C(15)	21(2)	40(2)	46(2)	8(2)	-5(2)	12(2)
C(16)	17(1)	27(2)	30(2)	5(1)	1(1)	10(1)
C(17)	28(2)	35(2)	42(2)	5(2)	10(2)	17(2)
C(18)	36(2)	40(2)	55(2)	7(2)	12(2)	25(2)
C(19)	30(2)	33(2)	32(2)	5(1)	-2(1)	20(2)
C(20)	42(2)	29(2)	43(2)	5(2)	-4(2)	22(2)
C(21)	35(2)	25(2)	39(2)	11(2)	-6(2)	12(2)
C(22)	24(2)	28(2)	26(2)	11(1)	-2(1)	9(1)
C(23)	21(1)	27(2)	21(1)	9(1)	-3(1)	11(1)
C(24)	21(1)	27(2)	28(2)	6(1)	-2(1)	13(1)
C(25)	19(1)	30(2)	16(1)	5(1)	-1(1)	6(1)
C(26)	20(1)	26(2)	27(2)	-2(1)	8(1)	8(1)
C(27)	31(2)	43(2)	37(2)	-17(2)	1(2)	15(2)
C(28)	44(2)	46(2)	51(3)	-24(2)	2(2)	13(2)
C(29)	59(3)	31(2)	52(3)	-6(2)	21(2)	18(2)
C(30)	48(2)	34(2)	45(2)	7(2)	20(2)	24(2)
C(31)	30(2)	30(2)	28(2)	2(1)	8(1)	14(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for p15103.

	x	y	z	U(eq)
H(2)	6114	9283	5206	35
H(3)	6779	8861	6376	51
H(4)	6527	9024	7940	63
H(5)	5592	9601	8370	53
H(7A)	3111	8262	5075	22
H(7B)	2838	9028	4907	22
H(10)	2131	6730	4616	32
H(11)	720	5573	4089	41
H(12)	-343	5931	3491	40
H(14A)	-612	7599	3777	49
H(14B)	-418	7411	2728	49
H(15A)	287	9089	3300	45
H(15B)	858	8832	2590	45
H(17A)	299	8738	4973	42
H(17B)	1258	8985	5442	42
H(18A)	790	10224	4589	49
H(18B)	1415	10405	5496	49
H(20)	2726	11888	4444	43
H(21)	3975	12226	3491	42
H(22)	4111	11077	2797	33
H(25A)	3367	9502	2205	29
H(25B)	2418	8743	2646	29
H(27)	2473	7549	2224	46
H(28)	2252	6117	1828	61
H(29)	3177	5605	2456	60
H(30)	4331	6520	3497	49
H(31)	4553	7959	3906	36

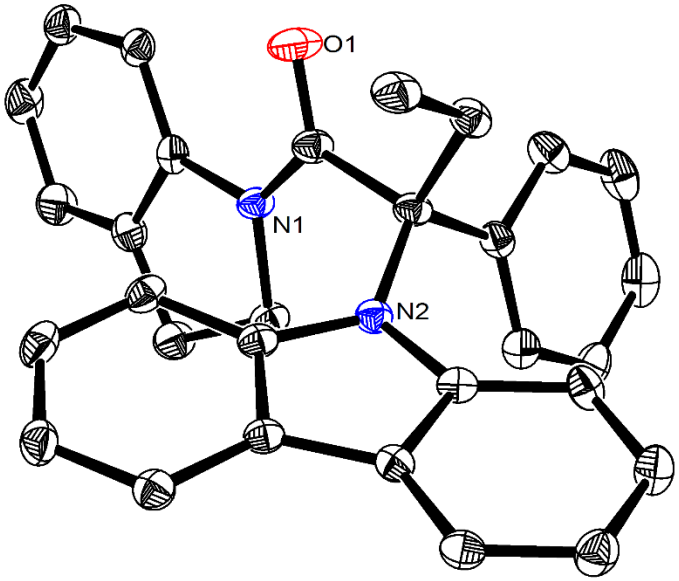


Fig. S3. Fig. 2B, Entry 1; structure determined by X-ray diffraction. One of two molecules in the asymmetric unit is shown. Ellipsoids are shown at 50% probability level, and H atoms have been omitted for clarity.

(*S*)-2-(Carbazol-9-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2B, Entry 1; 2). X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in hexanes of a sample synthesized with (*S*)-**L***. A crystal of $C_{30}H_{26}N_2O$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2 (*36*), the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package (*37*) using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S7. Crystal data and structure refinement for crystal_02.

Identification code	crystal_02	
Empirical formula	$C_{30}H_{26}N_2O$	
Formula weight	430.53	
Temperature	100.15 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.7927(4) Å	α = 90°.
	b = 14.9886(8) Å	β = 90 °.
	c = 19.0603(10) Å	γ = 90 °.
Volume	2226.3(2) $Å^3$	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.604 mm^{-1}	
F(000)	912	
Crystal size	0.23 x 0.22 x 0.19 mm^3	
Theta range for data collection	3.752 to 79.126°.	
Index ranges	-8<=h<=9, -18<=k<=18, -24<=l<=24	
Reflections collected	64505	
Independent reflections	4772 [R(int) = 0.0521]	
Completeness to theta = 67.679°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7328 and 0.6567	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4772 / 0 / 299	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1097	
R indices (all data)	R1 = 0.0427, wR2 = 0.1099	
Absolute structure parameter	0.08(9)	
Largest diff. peak and hole	0.267 and -0.279 $e/Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal_02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-6215(3)	-5806(1)	-1910(1)	31(1)
N(1)	-4132(3)	-5199(1)	-1243(1)	18(1)
N(2)	-6732(3)	-3620(1)	-1327(1)	17(1)
C(1)	-5521(3)	-5141(2)	-1677(1)	20(1)
C(2)	-6172(3)	-4200(2)	-1919(1)	18(1)
C(3)	-3137(3)	-4452(2)	-929(1)	20(1)
C(4)	-1987(4)	-4886(2)	-371(1)	26(1)
C(5)	-2123(3)	-5867(2)	-524(1)	22(1)
C(6)	-1187(4)	-6565(2)	-244(2)	28(1)
C(7)	-1583(4)	-7437(2)	-446(2)	30(1)
C(8)	-2903(4)	-7589(2)	-912(1)	26(1)
C(9)	-3872(3)	-6889(2)	-1202(1)	20(1)
C(10)	-3430(3)	-6028(2)	-1009(1)	18(1)
C(11)	-7734(3)	-4354(2)	-2411(1)	21(1)
C(12)	-9388(3)	-4603(2)	-2028(1)	24(1)
C(13)	-4663(3)	-3792(2)	-2334(1)	19(1)
C(14)	-3752(3)	-3039(2)	-2118(1)	21(1)
C(15)	-2413(4)	-2696(2)	-2516(1)	25(1)
C(16)	-1963(4)	-3097(2)	-3144(2)	30(1)
C(17)	-2837(4)	-3853(2)	-3364(1)	30(1)
C(18)	-4173(4)	-4198(2)	-2964(1)	25(1)
C(19)	-7337(3)	-3891(2)	-662(1)	17(1)
C(20)	-7132(3)	-4685(2)	-280(1)	19(1)
C(21)	-7787(3)	-4723(2)	398(1)	23(1)
C(22)	-8680(3)	-4011(2)	704(1)	22(1)
C(23)	-8961(3)	-3241(2)	321(1)	19(1)
C(24)	-8292(3)	-3185(2)	-360(1)	16(1)
C(25)	-8389(3)	-2488(2)	-875(1)	16(1)
C(26)	-9231(3)	-1665(2)	-880(1)	19(1)
C(27)	-9124(3)	-1134(2)	-1473(1)	23(1)
C(28)	-8182(3)	-1423(2)	-2056(1)	23(1)
C(29)	-7357(3)	-2238(2)	-2065(1)	20(1)
C(30)	-7453(3)	-2776(2)	-1462(1)	17(1)

Table S9. Bond lengths [Å] and angles [°] for crystal_02.

O(1)-C(1)	1.218(3)
N(1)-C(1)	1.364(3)
N(1)-C(3)	1.488(3)
N(1)-C(10)	1.428(3)
N(2)-C(2)	1.489(3)
N(2)-C(19)	1.412(3)
N(2)-C(30)	1.408(3)
C(1)-C(2)	1.569(3)
C(2)-C(11)	1.554(3)
C(2)-C(13)	1.543(3)
C(3)-C(4)	1.537(3)
C(4)-C(5)	1.502(4)
C(5)-C(6)	1.382(4)
C(5)-C(10)	1.397(3)
C(6)-C(7)	1.397(4)
C(7)-C(8)	1.378(4)
C(8)-C(9)	1.405(4)
C(9)-C(10)	1.385(3)
C(11)-C(12)	1.527(4)
C(13)-C(14)	1.396(4)
C(13)-C(18)	1.401(3)
C(14)-C(15)	1.389(4)
C(15)-C(16)	1.384(4)
C(16)-C(17)	1.387(4)
C(17)-C(18)	1.390(4)
C(19)-C(20)	1.404(3)
C(19)-C(24)	1.416(3)
C(20)-C(21)	1.390(4)
C(21)-C(22)	1.401(4)
C(22)-C(23)	1.383(3)
C(23)-C(24)	1.401(3)
C(24)-C(25)	1.436(3)
C(25)-C(26)	1.396(3)
C(25)-C(30)	1.405(3)
C(26)-C(27)	1.385(3)
C(27)-C(28)	1.400(3)
C(28)-C(29)	1.381(3)
C(29)-C(30)	1.406(3)
C(1)-N(1)-C(3)	127.5(2)
C(1)-N(1)-C(10)	123.2(2)

C(10)-N(1)-C(3)	109.25(19)
C(19)-N(2)-C(2)	127.63(19)
C(30)-N(2)-C(2)	120.15(19)
C(30)-N(2)-C(19)	106.80(19)
O(1)-C(1)-N(1)	121.4(2)
O(1)-C(1)-C(2)	119.0(2)
N(1)-C(1)-C(2)	119.5(2)
N(2)-C(2)-C(1)	113.37(19)
N(2)-C(2)-C(11)	108.34(19)
N(2)-C(2)-C(13)	112.33(18)
C(11)-C(2)-C(1)	107.31(19)
C(13)-C(2)-C(1)	105.10(19)
C(13)-C(2)-C(11)	110.26(19)
N(1)-C(3)-C(4)	105.23(19)
C(5)-C(4)-C(3)	103.8(2)
C(6)-C(5)-C(4)	128.9(2)
C(6)-C(5)-C(10)	120.7(2)
C(10)-C(5)-C(4)	110.4(2)
C(5)-C(6)-C(7)	119.0(3)
C(8)-C(7)-C(6)	119.8(2)
C(7)-C(8)-C(9)	122.1(2)
C(10)-C(9)-C(8)	117.3(2)
C(5)-C(10)-N(1)	109.6(2)
C(9)-C(10)-N(1)	129.2(2)
C(9)-C(10)-C(5)	121.1(2)
C(12)-C(11)-C(2)	114.1(2)
C(14)-C(13)-C(2)	123.9(2)
C(14)-C(13)-C(18)	117.8(2)
C(18)-C(13)-C(2)	118.4(2)
C(15)-C(14)-C(13)	121.3(2)
C(16)-C(15)-C(14)	120.2(3)
C(15)-C(16)-C(17)	119.4(3)
C(16)-C(17)-C(18)	120.4(2)
C(17)-C(18)-C(13)	120.9(3)
N(2)-C(19)-C(24)	109.1(2)
C(20)-C(19)-N(2)	132.1(2)
C(20)-C(19)-C(24)	118.8(2)
C(21)-C(20)-C(19)	118.4(2)
C(20)-C(21)-C(22)	122.5(2)
C(23)-C(22)-C(21)	119.7(2)
C(22)-C(23)-C(24)	118.7(2)
C(19)-C(24)-C(25)	107.1(2)
C(23)-C(24)-C(19)	121.9(2)

C(23)-C(24)-C(25)	131.1(2)
C(26)-C(25)-C(24)	132.3(2)
C(26)-C(25)-C(30)	120.6(2)
C(30)-C(25)-C(24)	107.1(2)
C(27)-C(26)-C(25)	119.0(2)
C(26)-C(27)-C(28)	120.1(2)
C(29)-C(28)-C(27)	121.9(2)
C(28)-C(29)-C(30)	118.1(2)
C(25)-C(30)-N(2)	109.7(2)
C(25)-C(30)-C(29)	120.2(2)
C(29)-C(30)-N(2)	130.1(2)

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal_02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	35(1)	17(1)	42(1)	-7(1)	-19(1)	2(1)
N(1)	19(1)	14(1)	21(1)	-2(1)	-3(1)	2(1)
N(2)	17(1)	16(1)	17(1)	-2(1)	-1(1)	1(1)
C(1)	19(1)	17(1)	24(1)	-4(1)	-3(1)	3(1)
C(2)	17(1)	16(1)	19(1)	-3(1)	-3(1)	2(1)
C(3)	16(1)	19(1)	26(1)	-1(1)	-5(1)	-2(1)
C(4)	26(1)	24(1)	29(1)	0(1)	-10(1)	1(1)
C(5)	21(1)	25(1)	21(1)	2(1)	-2(1)	2(1)
C(6)	29(1)	28(1)	29(1)	2(1)	-7(1)	6(1)
C(7)	35(2)	25(1)	29(1)	5(1)	-1(1)	10(1)
C(8)	34(2)	19(1)	25(1)	1(1)	5(1)	4(1)
C(9)	22(1)	19(1)	20(1)	1(1)	5(1)	1(1)
C(10)	17(1)	20(1)	17(1)	2(1)	3(1)	5(1)
C(11)	20(1)	22(1)	20(1)	-2(1)	-5(1)	4(1)
C(12)	18(1)	26(1)	28(1)	-3(1)	-9(1)	-1(1)
C(13)	21(1)	19(1)	16(1)	-1(1)	1(1)	6(1)
C(14)	19(1)	22(1)	22(1)	0(1)	3(1)	4(1)
C(15)	20(1)	23(1)	32(1)	7(1)	1(1)	3(1)
C(16)	24(1)	37(2)	29(1)	10(1)	7(1)	10(1)
C(17)	28(1)	42(2)	19(1)	1(1)	7(1)	14(1)
C(18)	24(1)	29(1)	21(1)	-4(1)	-1(1)	8(1)
C(19)	13(1)	17(1)	20(1)	-2(1)	-3(1)	-2(1)
C(20)	17(1)	16(1)	26(1)	1(1)	-4(1)	-2(1)
C(21)	20(1)	20(1)	29(1)	8(1)	-6(1)	-6(1)
C(22)	23(1)	25(1)	20(1)	4(1)	-1(1)	-6(1)
C(23)	16(1)	20(1)	20(1)	-1(1)	0(1)	-3(1)
C(24)	13(1)	16(1)	19(1)	-2(1)	-2(1)	-2(1)
C(25)	13(1)	19(1)	16(1)	-1(1)	0(1)	-2(1)
C(26)	18(1)	20(1)	20(1)	-4(1)	2(1)	2(1)
C(27)	23(1)	20(1)	25(1)	1(1)	2(1)	4(1)
C(28)	23(1)	23(1)	22(1)	5(1)	3(1)	4(1)
C(29)	19(1)	26(1)	15(1)	1(1)	1(1)	3(1)
C(30)	13(1)	17(1)	19(1)	-3(1)	0(1)	1(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal_02.

	x	y	z	U(eq)
H(3A)	-3916	-4008	-713	24
H(3B)	-2434	-4149	-1291	24
H(4A)	-787	-4678	-415	31
H(4B)	-2406	-4750	108	31
H(6)	-287	-6453	80	34
H(7)	-944	-7924	-263	36
H(8)	-3166	-8185	-1042	31
H(9)	-4793	-7002	-1516	24
H(11A)	-7938	-3804	-2686	25
H(11B)	-7447	-4836	-2746	25
H(12A)	-10300	-4711	-2371	36
H(12B)	-9726	-4112	-1717	36
H(12C)	-9198	-5143	-1750	36
H(14)	-4053	-2754	-1690	25
H(15)	-1804	-2186	-2358	30
H(16)	-1063	-2856	-3422	36
H(17)	-2521	-4136	-3791	36
H(18)	-4760	-4717	-3120	30
H(20)	-6559	-5183	-479	23
H(21)	-7622	-5252	664	27
H(22)	-9091	-4057	1172	27
H(23)	-9594	-2759	516	23
H(26)	-9867	-1473	-483	23
H(27)	-9691	-573	-1485	27
H(28)	-8109	-1048	-2456	28
H(29)	-6741	-2430	-2468	24

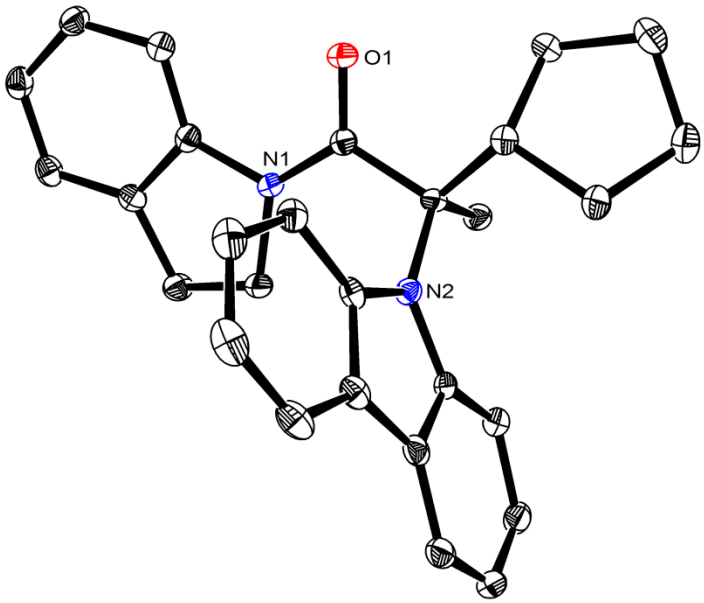


Fig. S4. Fig. 2B, Entry 5; structure determined by X-ray diffraction. One of two molecules in the asymmetric unit is shown. Ellipsoids are shown at 50% probability level, and H atoms have been omitted for clarity.

(*R*)-2-(Carbazol-9-yl)-2-cyclopentyl-1-(indolin-1-yl)propan-1-one (Fig. 2B, Entry 5; 3). X-ray quality crystals were obtained by slow diffusion of pentane into a saturated solution in benzene of a sample synthesized with (*S*)-**L***. A crystal of $C_{28}H_{28}N_2O$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon CMOS diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2 (*36*), the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package (*37*) using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S12. Crystal data and structure refinement for P15318.

Identification code	P15318	
Empirical formula	$C_{28}H_{28}N_2O$	
Formula weight	408.52	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.6751(3) Å	α = 90°.
	b = 18.0248(5) Å	β = 90 °.
	c = 20.3121(5) Å	γ = 90 °.
Volume	4274.51(19) $Å^3$	
Z	8	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.596 mm^{-1}	
F(000)	1744	
Crystal size	0.2 x 0.15 x 0.1 mm^3	
Theta range for data collection	3.278 to 70.105°.	
Index ranges	-14<=h<=8, -21<=k<=21, -24<=l<=24	
Reflections collected	38560	
Independent reflections	8073 [R(int) = 0.0452]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6918	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8073 / 0 / 561	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0700	
R indices (all data)	R1 = 0.0352, wR2 = 0.0719	
Absolute structure parameter	0.10(9)	
Largest diff. peak and hole	0.160 and -0.207 $e/Å^{-3}$	

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for P15318. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6831(1)	11992(1)	2174(1)	19(1)
N(1)	7856(1)	11515(1)	1331(1)	15(1)
N(2)	6981(1)	12821(1)	621(1)	14(1)
C(1)	7022(2)	11963(1)	1580(1)	14(1)
C(2)	6254(2)	12418(1)	1102(1)	14(1)
C(3)	5448(2)	11854(1)	781(1)	17(1)
C(4)	5553(2)	13003(1)	1498(1)	17(1)
C(5)	4881(2)	13534(1)	1033(1)	21(1)
C(6)	3628(2)	13494(1)	1253(1)	23(1)
C(7)	3707(2)	13302(1)	1982(1)	24(1)
C(8)	4646(2)	12710(1)	1988(1)	20(1)
C(9)	8245(2)	11444(1)	633(1)	18(1)
C(10)	9045(2)	10771(1)	632(1)	19(1)
C(11)	9343(2)	10669(1)	1346(1)	16(1)
C(12)	8609(2)	11090(1)	1740(1)	15(1)
C(13)	8697(2)	11072(1)	2422(1)	20(1)
C(14)	9560(2)	10639(1)	2696(1)	21(1)
C(15)	10315(2)	10238(1)	2308(1)	20(1)
C(16)	10200(2)	10250(1)	1626(1)	19(1)
C(17)	7861(2)	13293(1)	826(1)	15(1)
C(18)	8391(2)	13349(1)	1442(1)	18(1)
C(19)	9320(2)	13827(1)	1498(1)	22(1)
C(20)	9704(2)	14254(1)	966(1)	24(1)
C(21)	9167(2)	14207(1)	362(1)	22(1)
C(22)	8244(2)	13719(1)	290(1)	16(1)
C(23)	7577(2)	13497(1)	-273(1)	16(1)
C(24)	7629(2)	13709(1)	-935(1)	20(1)
C(25)	6928(2)	13359(1)	-1385(1)	22(1)
C(26)	6174(2)	12808(1)	-1174(1)	21(1)
C(27)	6096(2)	12591(1)	-520(1)	17(1)
C(28)	6811(2)	12938(1)	-60(1)	14(1)
O(2)	6429(1)	9881(1)	551(1)	18(1)
N(3)	5317(1)	9042(1)	1076(1)	15(1)
N(4)	6720(1)	7947(1)	433(1)	15(1)
C(29)	6080(2)	9242(1)	602(1)	15(1)
C(30)	6456(2)	8652(1)	88(1)	15(1)
C(31)	5455(2)	8600(1)	-402(1)	17(1)
C(32)	7567(2)	8901(1)	-271(1)	15(1)

C(33)	7493(2)	9526(1)	-780(1)	18(1)
C(34)	8661(2)	9480(1)	-1121(1)	21(1)
C(35)	8920(2)	8642(1)	-1170(1)	20(1)
C(36)	8128(2)	8262(1)	-662(1)	18(1)
C(37)	4753(2)	8311(1)	1183(1)	19(1)
C(38)	3647(2)	8507(1)	1554(1)	22(1)
C(39)	3953(2)	9229(1)	1881(1)	18(1)
C(40)	4916(2)	9534(1)	1578(1)	15(1)
C(41)	5388(2)	10201(1)	1791(1)	17(1)
C(42)	4848(2)	10565(1)	2311(1)	21(1)
C(43)	3880(2)	10270(1)	2610(1)	23(1)
C(44)	3434(2)	9596(1)	2399(1)	22(1)
C(45)	6518(2)	7213(1)	236(1)	15(1)
C(46)	5802(2)	6914(1)	-251(1)	19(1)
C(47)	5775(2)	6151(1)	-327(1)	24(1)
C(48)	6437(2)	5676(1)	63(1)	26(1)
C(49)	7132(2)	5962(1)	546(1)	22(1)
C(50)	7165(2)	6731(1)	641(1)	17(1)
C(51)	7797(2)	7188(1)	1094(1)	17(1)
C(52)	8569(2)	7022(1)	1601(1)	22(1)
C(53)	9074(2)	7600(1)	1942(1)	24(1)
C(54)	8804(2)	8334(1)	1790(1)	22(1)
C(55)	8025(2)	8514(1)	1301(1)	18(1)
C(56)	7520(2)	7932(1)	948(1)	15(1)

Table S14. Bond lengths [Å] and angles [°] for P15318.

O(1)-C(1)	1.228(2)
N(1)-C(1)	1.364(3)
N(1)-C(9)	1.494(2)
N(1)-C(12)	1.431(2)
N(2)-C(2)	1.486(2)
N(2)-C(17)	1.398(3)
N(2)-C(28)	1.412(2)
C(1)-C(2)	1.554(3)
C(2)-C(3)	1.531(3)
C(2)-C(4)	1.558(3)
C(4)-C(5)	1.557(3)
C(4)-C(8)	1.546(3)
C(5)-C(6)	1.532(3)
C(6)-C(7)	1.524(3)
C(7)-C(8)	1.531(3)
C(9)-C(10)	1.532(3)
C(10)-C(11)	1.502(3)
C(11)-C(12)	1.396(3)
C(11)-C(16)	1.377(3)
C(12)-C(13)	1.390(3)
C(13)-C(14)	1.391(3)
C(14)-C(15)	1.385(3)
C(15)-C(16)	1.391(3)
C(17)-C(18)	1.400(3)
C(17)-C(22)	1.406(3)
C(18)-C(19)	1.390(3)
C(19)-C(20)	1.400(3)
C(20)-C(21)	1.379(3)
C(21)-C(22)	1.399(3)
C(22)-C(23)	1.440(3)
C(23)-C(24)	1.399(3)
C(23)-C(28)	1.417(3)
C(24)-C(25)	1.379(3)
C(25)-C(26)	1.394(3)
C(26)-C(27)	1.389(3)
C(27)-C(28)	1.401(3)
O(2)-C(29)	1.225(2)
N(3)-C(29)	1.361(3)
N(3)-C(37)	1.489(2)
N(3)-C(40)	1.429(2)
N(4)-C(30)	1.484(2)

N(4)-C(45)	1.402(3)
N(4)-C(56)	1.402(3)
C(29)-C(30)	1.554(3)
C(30)-C(31)	1.538(3)
C(30)-C(32)	1.554(3)
C(32)-C(33)	1.532(3)
C(32)-C(36)	1.545(3)
C(33)-C(34)	1.531(3)
C(34)-C(35)	1.543(3)
C(35)-C(36)	1.546(3)
C(37)-C(38)	1.537(3)
C(38)-C(39)	1.504(3)
C(39)-C(40)	1.395(3)
C(39)-C(44)	1.381(3)
C(40)-C(41)	1.392(3)
C(41)-C(42)	1.394(3)
C(42)-C(43)	1.389(3)
C(43)-C(44)	1.390(3)
C(45)-C(46)	1.404(3)
C(45)-C(50)	1.414(3)
C(46)-C(47)	1.384(3)
C(47)-C(48)	1.399(3)
C(48)-C(49)	1.375(3)
C(49)-C(50)	1.401(3)
C(50)-C(51)	1.438(3)
C(51)-C(52)	1.401(3)
C(51)-C(56)	1.410(3)
C(52)-C(53)	1.382(3)
C(53)-C(54)	1.394(3)
C(54)-C(55)	1.386(3)
C(55)-C(56)	1.401(3)

C(1)-N(1)-C(9)	128.29(16)
C(1)-N(1)-C(12)	122.70(16)
C(12)-N(1)-C(9)	108.59(15)
C(17)-N(2)-C(2)	121.44(16)
C(17)-N(2)-C(28)	107.80(16)
C(28)-N(2)-C(2)	129.53(16)
O(1)-C(1)-N(1)	121.29(18)
O(1)-C(1)-C(2)	119.13(17)
N(1)-C(1)-C(2)	119.50(16)
N(2)-C(2)-C(1)	109.85(15)
N(2)-C(2)-C(3)	113.33(16)

N(2)-C(2)-C(4)	107.93(15)
C(1)-C(2)-C(4)	109.74(15)
C(3)-C(2)-C(1)	105.75(15)
C(3)-C(2)-C(4)	110.22(16)
C(5)-C(4)-C(2)	111.61(16)
C(8)-C(4)-C(2)	117.39(17)
C(8)-C(4)-C(5)	104.86(16)
C(6)-C(5)-C(4)	105.91(17)
C(7)-C(6)-C(5)	103.72(17)
C(6)-C(7)-C(8)	102.07(17)
C(7)-C(8)-C(4)	104.32(17)
N(1)-C(9)-C(10)	104.64(16)
C(11)-C(10)-C(9)	103.72(16)
C(12)-C(11)-C(10)	110.18(17)
C(16)-C(11)-C(10)	129.36(19)
C(16)-C(11)-C(12)	120.45(19)
C(11)-C(12)-N(1)	109.55(17)
C(13)-C(12)-N(1)	129.50(18)
C(13)-C(12)-C(11)	120.93(19)
C(12)-C(13)-C(14)	117.7(2)
C(15)-C(14)-C(13)	121.8(2)
C(14)-C(15)-C(16)	119.77(19)
C(11)-C(16)-C(15)	119.34(19)
N(2)-C(17)-C(18)	129.48(18)
N(2)-C(17)-C(22)	109.53(17)
C(18)-C(17)-C(22)	120.88(18)
C(19)-C(18)-C(17)	117.49(19)
C(18)-C(19)-C(20)	121.9(2)
C(21)-C(20)-C(19)	120.5(2)
C(20)-C(21)-C(22)	118.8(2)
C(17)-C(22)-C(23)	106.97(17)
C(21)-C(22)-C(17)	120.43(19)
C(21)-C(22)-C(23)	132.5(2)
C(24)-C(23)-C(22)	131.59(19)
C(24)-C(23)-C(28)	121.08(19)
C(28)-C(23)-C(22)	107.23(17)
C(25)-C(24)-C(23)	119.07(19)
C(24)-C(25)-C(26)	119.85(19)
C(27)-C(26)-C(25)	122.4(2)
C(26)-C(27)-C(28)	118.30(19)
N(2)-C(28)-C(23)	108.46(17)
C(27)-C(28)-N(2)	132.19(19)
C(27)-C(28)-C(23)	119.29(18)

C(29)-N(3)-C(37)	128.75(16)
C(29)-N(3)-C(40)	123.71(16)
C(40)-N(3)-C(37)	107.53(15)
C(45)-N(4)-C(30)	129.60(16)
C(56)-N(4)-C(30)	120.57(16)
C(56)-N(4)-C(45)	107.83(16)
O(2)-C(29)-N(3)	121.71(18)
O(2)-C(29)-C(30)	119.54(18)
N(3)-C(29)-C(30)	118.65(17)
N(4)-C(30)-C(29)	109.09(15)
N(4)-C(30)-C(31)	114.34(16)
N(4)-C(30)-C(32)	107.18(15)
C(29)-C(30)-C(32)	110.65(16)
C(31)-C(30)-C(29)	105.22(16)
C(31)-C(30)-C(32)	110.38(16)
C(33)-C(32)-C(30)	118.86(16)
C(33)-C(32)-C(36)	103.00(16)
C(36)-C(32)-C(30)	112.28(16)
C(34)-C(33)-C(32)	102.43(16)
C(33)-C(34)-C(35)	104.91(16)
C(34)-C(35)-C(36)	105.85(16)
C(32)-C(36)-C(35)	105.45(16)
N(3)-C(37)-C(38)	103.79(15)
C(39)-C(38)-C(37)	102.54(16)
C(40)-C(39)-C(38)	109.67(18)
C(44)-C(39)-C(38)	130.26(19)
C(44)-C(39)-C(40)	120.06(19)
C(39)-C(40)-N(3)	109.56(17)
C(41)-C(40)-N(3)	128.95(18)
C(41)-C(40)-C(39)	121.41(19)
C(40)-C(41)-C(42)	117.64(19)
C(43)-C(42)-C(41)	121.3(2)
C(42)-C(43)-C(44)	120.2(2)
C(39)-C(44)-C(43)	119.4(2)
N(4)-C(45)-C(46)	131.64(18)
N(4)-C(45)-C(50)	108.91(17)
C(46)-C(45)-C(50)	119.43(18)
C(47)-C(46)-C(45)	118.3(2)
C(46)-C(47)-C(48)	122.2(2)
C(49)-C(48)-C(47)	120.0(2)
C(48)-C(49)-C(50)	119.0(2)
C(45)-C(50)-C(51)	107.08(17)
C(49)-C(50)-C(45)	121.0(2)

C(49)-C(50)-C(51)	132.0(2)
C(52)-C(51)-C(50)	132.69(19)
C(52)-C(51)-C(56)	120.33(19)
C(56)-C(51)-C(50)	106.98(18)
C(53)-C(52)-C(51)	118.76(19)
C(52)-C(53)-C(54)	120.6(2)
C(55)-C(54)-C(53)	121.9(2)
C(54)-C(55)-C(56)	117.9(2)
N(4)-C(56)-C(51)	109.17(17)
C(55)-C(56)-N(4)	130.30(18)
C(55)-C(56)-C(51)	120.53(18)

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for P15318. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	24(1)	13(1)	1(1)	1(1)	4(1)
N(1)	16(1)	17(1)	12(1)	0(1)	-1(1)	1(1)
N(2)	13(1)	14(1)	14(1)	0(1)	-1(1)	-1(1)
C(1)	14(1)	15(1)	14(1)	0(1)	-1(1)	-3(1)
C(2)	14(1)	16(1)	12(1)	1(1)	2(1)	-1(1)
C(3)	16(1)	19(1)	15(1)	1(1)	-1(1)	-2(1)
C(4)	16(1)	18(1)	17(1)	1(1)	0(1)	2(1)
C(5)	20(1)	20(1)	22(1)	2(1)	0(1)	5(1)
C(6)	18(1)	20(1)	30(1)	2(1)	-3(1)	4(1)
C(7)	19(1)	27(1)	27(1)	-5(1)	4(1)	2(1)
C(8)	18(1)	26(1)	17(1)	1(1)	3(1)	3(1)
C(9)	19(1)	20(1)	13(1)	1(1)	1(1)	3(1)
C(10)	23(1)	18(1)	16(1)	-1(1)	1(1)	4(1)
C(11)	16(1)	14(1)	18(1)	1(1)	2(1)	-3(1)
C(12)	14(1)	14(1)	18(1)	2(1)	-2(1)	-3(1)
C(13)	18(1)	22(1)	18(1)	1(1)	0(1)	2(1)
C(14)	20(1)	24(1)	18(1)	5(1)	-2(1)	-2(1)
C(15)	17(1)	17(1)	25(1)	5(1)	-2(1)	0(1)
C(16)	17(1)	16(1)	24(1)	0(1)	2(1)	1(1)
C(17)	12(1)	13(1)	19(1)	-2(1)	2(1)	1(1)
C(18)	18(1)	17(1)	18(1)	-4(1)	-1(1)	1(1)
C(19)	20(1)	21(1)	25(1)	-10(1)	-3(1)	1(1)
C(20)	19(1)	17(1)	36(1)	-9(1)	2(1)	-4(1)
C(21)	20(1)	16(1)	29(1)	-4(1)	8(1)	-1(1)
C(22)	17(1)	11(1)	22(1)	-2(1)	4(1)	3(1)
C(23)	15(1)	15(1)	20(1)	1(1)	3(1)	4(1)
C(24)	18(1)	18(1)	22(1)	6(1)	5(1)	5(1)
C(25)	22(1)	28(1)	16(1)	5(1)	2(1)	7(1)
C(26)	20(1)	26(1)	17(1)	-1(1)	-3(1)	6(1)
C(27)	16(1)	19(1)	17(1)	1(1)	-1(1)	1(1)
C(28)	14(1)	15(1)	15(1)	1(1)	1(1)	5(1)
O(2)	22(1)	14(1)	19(1)	0(1)	4(1)	-2(1)
N(3)	17(1)	13(1)	16(1)	-2(1)	2(1)	-2(1)
N(4)	16(1)	14(1)	15(1)	0(1)	-2(1)	0(1)
C(29)	14(1)	16(1)	16(1)	1(1)	-2(1)	1(1)
C(30)	16(1)	13(1)	14(1)	0(1)	-1(1)	0(1)
C(31)	17(1)	16(1)	17(1)	1(1)	-2(1)	0(1)
C(32)	16(1)	14(1)	14(1)	0(1)	0(1)	0(1)

C(33)	20(1)	17(1)	17(1)	2(1)	1(1)	4(1)
C(34)	24(1)	19(1)	20(1)	4(1)	6(1)	0(1)
C(35)	20(1)	21(1)	18(1)	-1(1)	4(1)	2(1)
C(36)	19(1)	16(1)	19(1)	1(1)	2(1)	2(1)
C(37)	20(1)	14(1)	23(1)	0(1)	5(1)	-4(1)
C(38)	16(1)	22(1)	28(1)	-1(1)	3(1)	-3(1)
C(39)	15(1)	18(1)	21(1)	2(1)	0(1)	2(1)
C(40)	17(1)	15(1)	14(1)	1(1)	0(1)	3(1)
C(41)	19(1)	18(1)	15(1)	2(1)	-1(1)	1(1)
C(42)	29(1)	18(1)	16(1)	-1(1)	-2(1)	2(1)
C(43)	28(1)	24(1)	18(1)	-1(1)	5(1)	8(1)
C(44)	19(1)	24(1)	22(1)	5(1)	6(1)	5(1)
C(45)	15(1)	14(1)	17(1)	0(1)	5(1)	1(1)
C(46)	18(1)	18(1)	20(1)	-3(1)	1(1)	-1(1)
C(47)	23(1)	20(1)	28(1)	-9(1)	2(1)	-2(1)
C(48)	30(1)	14(1)	34(1)	-3(1)	6(1)	0(1)
C(49)	23(1)	16(1)	28(1)	3(1)	6(1)	4(1)
C(50)	17(1)	17(1)	18(1)	2(1)	4(1)	2(1)
C(51)	16(1)	20(1)	15(1)	3(1)	5(1)	1(1)
C(52)	22(1)	25(1)	18(1)	7(1)	3(1)	6(1)
C(53)	19(1)	38(1)	15(1)	6(1)	-1(1)	4(1)
C(54)	20(1)	31(1)	15(1)	0(1)	0(1)	-3(1)
C(55)	19(1)	19(1)	15(1)	1(1)	1(1)	0(1)
C(56)	13(1)	19(1)	13(1)	2(1)	3(1)	1(1)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for P15318.

	x	y	z	U(eq)
H(3A)	4838	12118	545	25
H(3B)	5109	11538	1122	25
H(3C)	5880	11547	470	25
H(4)	6110	13311	1753	20
H(5A)	5175	14048	1072	25
H(5B)	4958	13373	569	25
H(6A)	3237	13976	1187	27
H(6B)	3208	13105	1008	27
H(7A)	2973	13102	2150	29
H(7B)	3929	13739	2248	29
H(8A)	4341	12224	1842	25
H(8B)	4978	12654	2434	25
H(9A)	8658	11897	490	21
H(9B)	7586	11363	335	21
H(10A)	8651	10327	456	23
H(10B)	9739	10868	366	23
H(13)	8185	11347	2692	23
H(14)	9635	10618	3161	25
H(15)	10909	9956	2507	24
H(16)	10708	9972	1357	22
H(18)	8126	13070	1809	21
H(19)	9707	13865	1908	27
H(20)	10337	14579	1021	29
H(21)	9420	14501	2	26
H(24)	8139	14089	-1073	24
H(25)	6959	13493	-1837	26
H(26)	5697	12573	-1490	25
H(27)	5572	12216	-389	21
H(31A)	5704	8330	-796	25
H(31B)	5209	9100	-527	25
H(31C)	4815	8335	-197	25
H(32)	8125	9061	74	18
H(33A)	6861	9440	-1096	22
H(33B)	7384	10014	-566	22
H(34A)	9255	9736	-858	25
H(34B)	8629	9708	-1564	25
H(35A)	9734	8543	-1066	23

H(35B)	8757	8457	-1619	23
H(36A)	7538	7959	-886	21
H(36B)	8576	7937	-365	21
H(37A)	5245	7978	1448	23
H(37B)	4579	8066	758	23
H(38A)	2995	8569	1248	26
H(38B)	3454	8122	1884	26
H(41)	6054	10401	1590	21
H(42)	5147	11024	2464	25
H(43)	3520	10531	2961	28
H(44)	2780	9389	2608	26
H(46)	5348	7227	-522	23
H(47)	5290	5943	-654	28
H(48)	6406	5155	-7	31
H(49)	7584	5642	813	27
H(52)	8743	6522	1709	26
H(53)	9609	7496	2282	29
H(54)	9165	8722	2029	26
H(55)	7839	9016	1208	21

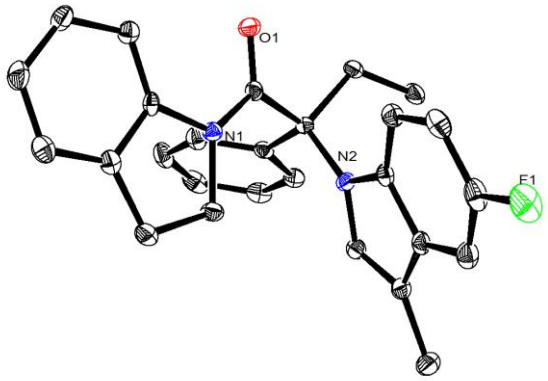


Fig. S5. Fig. 2C, Entry 9; structure determined by X-ray diffraction. One of two molecules in the asymmetric unit is shown. Ellipsoids are shown at 50% probability level, and H atoms have been omitted for clarity.

(*S*)-2-(5-Fluoro-3-methyl-indol-1-yl)-1-(indolin-1-yl)-2-phenylbutan-1-one (Fig. 2C, Entry 9; 4). X-ray quality crystals were obtained by slow diffusion of pentane into a saturated solution in benzene of a sample synthesized with (*S*)-**L***. A crystal of $C_{27}H_{25}FN_2O$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2 (*36*), the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package (*37*) using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S17. Crystal data and structure refinement for P15247.

Identification code	P15247	
Empirical formula	C27 H25 F N2 O	
Formula weight	412.49	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 35.820(2) Å	a= 90°.
	b = 6.2695(4) Å	b= 105.840(3)°.
	c = 19.1086(12) Å	g = 90°.
Volume	4128.4(4) $Å^3$	
Z	8	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.696 mm^{-1}	
F(000)	1744	
Crystal size	0.300 x 0.050 x 0.050 mm^3	
Theta range for data collection	2.403 to 79.586°.	
Index ranges	-45<=h<=44, -7<=k<=7, -24<=l<=24	
Reflections collected	38825	
Independent reflections	8771 [R(int) = 0.0580]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9891 and 0.9186	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8771 / 1 / 563	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0745	
R indices (all data)	R1 = 0.0425, wR2 = 0.0777	
Absolute structure parameter	0.05(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.176 and -0.222 $e.Å^{-3}$	

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for P15247. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3754(1)	3436(3)	2418(1)	19(1)
C(1)	3735(1)	1785(4)	2067(1)	14(1)
N(1)	4036(1)	369(3)	2201(1)	14(1)
C(2)	4366(1)	512(4)	2821(1)	14(1)
C(3)	4467(1)	2102(4)	3343(1)	17(1)
C(4)	4802(1)	1809(4)	3915(1)	21(1)
C(5)	5029(1)	-9(4)	3961(1)	24(1)
C(6)	4923(1)	-1580(4)	3428(1)	23(1)
C(7)	4591(1)	-1324(4)	2860(1)	17(1)
C(8)	4421(1)	-2806(4)	2240(1)	20(1)
C(9)	4043(1)	-1707(4)	1822(1)	17(1)
C(10)	3348(1)	1265(3)	1481(1)	13(1)
N(2)	3429(1)	494(3)	806(1)	14(1)
C(11)	3667(1)	1556(4)	453(1)	14(1)
C(12)	3889(1)	3410(4)	642(1)	17(1)
C(13)	4111(1)	4058(4)	190(1)	21(1)
C(14)	4110(1)	2854(4)	-424(1)	22(1)
F(1)	4336(1)	3559(3)	-848(1)	34(1)
C(15)	3900(1)	1032(4)	-621(1)	20(1)
C(16)	3668(1)	362(4)	-174(1)	16(1)
C(17)	3420(1)	-1436(4)	-205(1)	17(1)
C(19)	3320(1)	-3092(4)	-793(1)	23(1)
C(18)	3288(1)	-1305(4)	401(1)	15(1)
C(20)	3121(1)	-354(3)	1808(1)	15(1)
C(21)	2750(1)	-1059(4)	1421(1)	17(1)
C(22)	2533(1)	-2395(4)	1743(1)	22(1)
C(23)	2682(1)	-3068(4)	2458(2)	25(1)
C(24)	3046(1)	-2380(4)	2846(1)	24(1)
C(25)	3262(1)	-1035(4)	2528(1)	19(1)
C(26)	3119(1)	3401(4)	1317(1)	16(1)
C(27)	2775(1)	3412(4)	638(1)	21(1)
O(101)	3773(1)	7642(3)	7525(1)	21(1)
C(101)	3818(1)	9287(4)	7212(1)	14(1)
N(101)	4160(1)	10366(3)	7399(1)	15(1)
C(102)	4484(1)	9768(4)	7989(1)	16(1)
C(103)	4525(1)	8018(4)	8452(1)	20(1)
C(104)	4869(1)	7859(5)	9013(1)	25(1)
C(105)	5159(1)	9377(5)	9109(1)	30(1)

C(106)	5115(1)	11086(5)	8632(1)	26(1)
C(107)	4778(1)	11279(4)	8068(1)	19(1)
C(108)	4667(1)	12950(4)	7491(1)	22(1)
C(109)	4246(1)	12457(5)	7106(2)	34(1)
C(110)	3477(1)	10174(3)	6588(1)	14(1)
N(102)	3610(1)	10532(3)	5932(1)	14(1)
C(111)	3822(1)	9098(3)	5639(1)	14(1)
C(112)	4008(1)	7195(4)	5916(1)	16(1)
C(113)	4204(1)	6104(4)	5496(1)	20(1)
C(114)	4214(1)	6923(4)	4825(1)	21(1)
F(101)	4418(1)	5798(3)	4441(1)	30(1)
C(115)	4029(1)	8750(4)	4528(1)	20(1)
C(116)	3823(1)	9862(4)	4939(1)	16(1)
C(117)	3591(1)	11757(4)	4806(1)	17(1)
C(118)	3464(1)	12086(4)	5408(1)	16(1)
C(119)	3502(1)	13114(4)	4135(1)	24(1)
C(120)	3137(1)	8581(4)	6411(1)	15(1)
C(121)	2980(1)	7863(4)	5704(1)	18(1)
C(122)	2651(1)	6559(4)	5527(1)	22(1)
C(123)	2475(1)	5966(4)	6054(1)	22(1)
C(124)	2630(1)	6650(4)	6765(1)	20(1)
C(125)	2959(1)	7928(4)	6945(1)	17(1)
C(126)	3331(1)	12350(4)	6826(1)	16(1)
C(127)	3373(1)	12611(4)	7639(1)	20(1)

Table S19. Bond lengths [Å] and angles [°] for P15247.

O(1)-C(1)	1.225(3)
C(1)-N(1)	1.364(3)
C(1)-C(10)	1.560(3)
N(1)-C(2)	1.431(3)
N(1)-C(9)	1.493(3)
C(2)-C(3)	1.387(3)
C(2)-C(7)	1.394(3)
C(3)-C(4)	1.397(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.392(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.384(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.498(3)
C(8)-C(9)	1.536(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(2)	1.478(3)
C(10)-C(20)	1.538(3)
C(10)-C(26)	1.557(3)
N(2)-C(18)	1.384(3)
N(2)-C(11)	1.392(3)
C(11)-C(12)	1.398(3)
C(11)-C(16)	1.415(3)
C(12)-C(13)	1.385(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.395(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.364(4)
C(14)-F(1)	1.366(3)
C(15)-C(16)	1.407(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.426(3)
C(17)-C(18)	1.369(3)
C(17)-C(19)	1.499(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800

C(19)-H(19C)	0.9800
C(18)-H(18)	0.9500
C(20)-C(25)	1.396(3)
C(20)-C(21)	1.404(3)
C(21)-C(22)	1.394(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.390(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.382(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.392(3)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(26)-C(27)	1.528(3)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
O(101)-C(101)	1.225(3)
C(101)-N(101)	1.357(3)
C(101)-C(110)	1.559(3)
N(101)-C(102)	1.430(3)
N(101)-C(109)	1.490(3)
C(102)-C(103)	1.392(3)
C(102)-C(107)	1.394(3)
C(103)-C(104)	1.400(3)
C(103)-H(103)	0.9500
C(104)-C(105)	1.382(4)
C(104)-H(104)	0.9500
C(105)-C(106)	1.387(4)
C(105)-H(105)	0.9500
C(106)-C(107)	1.386(3)
C(106)-H(106)	0.9500
C(107)-C(108)	1.495(4)
C(108)-C(109)	1.516(3)
C(108)-H(10A)	0.9900
C(108)-H(10B)	0.9900
C(109)-H(10C)	0.9900
C(109)-H(10D)	0.9900
C(110)-N(102)	1.475(3)
C(110)-C(120)	1.539(3)
C(110)-C(126)	1.571(3)

N(102)-C(111)	1.391(3)
N(102)-C(118)	1.393(3)
C(111)-C(112)	1.398(3)
C(111)-C(116)	1.422(3)
C(112)-C(113)	1.384(3)
C(112)-H(112)	0.9500
C(113)-C(114)	1.391(3)
C(113)-H(113)	0.9500
C(114)-F(101)	1.365(3)
C(114)-C(115)	1.366(4)
C(115)-C(116)	1.402(3)
C(115)-H(115)	0.9500
C(116)-C(117)	1.433(3)
C(117)-C(118)	1.363(3)
C(117)-C(119)	1.499(3)
C(118)-H(118)	0.9500
C(119)-H(11A)	0.9800
C(119)-H(11B)	0.9800
C(119)-H(11C)	0.9800
C(120)-C(121)	1.389(3)
C(120)-C(125)	1.404(3)
C(121)-C(122)	1.396(3)
C(121)-H(121)	0.9500
C(122)-C(123)	1.379(3)
C(122)-H(122)	0.9500
C(123)-C(124)	1.387(4)
C(123)-H(123)	0.9500
C(124)-C(125)	1.388(3)
C(124)-H(124)	0.9500
C(125)-H(125)	0.9500
C(126)-C(127)	1.528(3)
C(126)-H(12A)	0.9900
C(126)-H(12B)	0.9900
C(127)-H(12C)	0.9800
C(127)-H(12D)	0.9800
C(127)-H(12E)	0.9800

O(1)-C(1)-N(1)	121.7(2)
O(1)-C(1)-C(10)	118.28(19)
N(1)-C(1)-C(10)	120.00(19)
C(1)-N(1)-C(2)	123.17(19)
C(1)-N(1)-C(9)	126.33(18)
C(2)-N(1)-C(9)	109.68(17)

C(3)-C(2)-C(7)	121.5(2)
C(3)-C(2)-N(1)	129.4(2)
C(7)-C(2)-N(1)	109.12(19)
C(2)-C(3)-C(4)	117.8(2)
C(2)-C(3)-H(3)	121.1
C(4)-C(3)-H(3)	121.1
C(5)-C(4)-C(3)	121.3(2)
C(5)-C(4)-H(4)	119.3
C(3)-C(4)-H(4)	119.3
C(4)-C(5)-C(6)	119.8(2)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(7)-C(6)-C(5)	119.6(2)
C(7)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
C(6)-C(7)-C(2)	119.9(2)
C(6)-C(7)-C(8)	128.7(2)
C(2)-C(7)-C(8)	111.46(19)
C(7)-C(8)-C(9)	104.07(18)
C(7)-C(8)-H(8A)	110.9
C(9)-C(8)-H(8A)	110.9
C(7)-C(8)-H(8B)	110.9
C(9)-C(8)-H(8B)	110.9
H(8A)-C(8)-H(8B)	109.0
N(1)-C(9)-C(8)	105.54(18)
N(1)-C(9)-H(9A)	110.6
C(8)-C(9)-H(9A)	110.6
N(1)-C(9)-H(9B)	110.6
C(8)-C(9)-H(9B)	110.6
H(9A)-C(9)-H(9B)	108.8
N(2)-C(10)-C(20)	113.02(17)
N(2)-C(10)-C(26)	108.93(17)
C(20)-C(10)-C(26)	109.88(17)
N(2)-C(10)-C(1)	110.31(16)
C(20)-C(10)-C(1)	108.15(17)
C(26)-C(10)-C(1)	106.33(17)
C(18)-N(2)-C(11)	107.35(17)
C(18)-N(2)-C(10)	128.71(18)
C(11)-N(2)-C(10)	123.92(18)
N(2)-C(11)-C(12)	130.7(2)
N(2)-C(11)-C(16)	107.55(19)
C(12)-C(11)-C(16)	121.7(2)
C(13)-C(12)-C(11)	117.8(2)

C(13)-C(12)-H(12)	121.1
C(11)-C(12)-H(12)	121.1
C(12)-C(13)-C(14)	119.7(2)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(15)-C(14)-F(1)	118.7(2)
C(15)-C(14)-C(13)	124.0(2)
F(1)-C(14)-C(13)	117.3(2)
C(14)-C(15)-C(16)	117.1(2)
C(14)-C(15)-H(15)	121.4
C(16)-C(15)-H(15)	121.4
C(15)-C(16)-C(11)	119.7(2)
C(15)-C(16)-C(17)	132.4(2)
C(11)-C(16)-C(17)	107.90(18)
C(18)-C(17)-C(16)	105.9(2)
C(18)-C(17)-C(19)	127.3(2)
C(16)-C(17)-C(19)	126.8(2)
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(18)-N(2)	111.28(19)
C(17)-C(18)-H(18)	124.4
N(2)-C(18)-H(18)	124.4
C(25)-C(20)-C(21)	117.4(2)
C(25)-C(20)-C(10)	120.8(2)
C(21)-C(20)-C(10)	121.5(2)
C(22)-C(21)-C(20)	121.1(2)
C(22)-C(21)-H(21)	119.5
C(20)-C(21)-H(21)	119.5
C(23)-C(22)-C(21)	120.5(2)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(24)-C(23)-C(22)	118.9(2)
C(24)-C(23)-H(23)	120.5
C(22)-C(23)-H(23)	120.5
C(23)-C(24)-C(25)	120.8(2)
C(23)-C(24)-H(24)	119.6
C(25)-C(24)-H(24)	119.6
C(24)-C(25)-C(20)	121.3(2)
C(24)-C(25)-H(25)	119.4

C(20)-C(25)-H(25)	119.4
C(27)-C(26)-C(10)	115.70(18)
C(27)-C(26)-H(26A)	108.4
C(10)-C(26)-H(26A)	108.4
C(27)-C(26)-H(26B)	108.4
C(10)-C(26)-H(26B)	108.4
H(26A)-C(26)-H(26B)	107.4
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
O(101)-C(101)-N(101)	121.4(2)
O(101)-C(101)-C(110)	119.5(2)
N(101)-C(101)-C(110)	119.05(19)
C(101)-N(101)-C(102)	123.73(19)
C(101)-N(101)-C(109)	127.24(19)
C(102)-N(101)-C(109)	108.60(18)
C(103)-C(102)-C(107)	121.4(2)
C(103)-C(102)-N(101)	129.1(2)
C(107)-C(102)-N(101)	109.5(2)
C(102)-C(103)-C(104)	117.5(2)
C(102)-C(103)-H(103)	121.3
C(104)-C(103)-H(103)	121.3
C(105)-C(104)-C(103)	121.7(2)
C(105)-C(104)-H(104)	119.2
C(103)-C(104)-H(104)	119.2
C(104)-C(105)-C(106)	119.8(2)
C(104)-C(105)-H(105)	120.1
C(106)-C(105)-H(105)	120.1
C(107)-C(106)-C(105)	119.8(2)
C(107)-C(106)-H(106)	120.1
C(105)-C(106)-H(106)	120.1
C(106)-C(107)-C(102)	119.8(2)
C(106)-C(107)-C(108)	129.4(2)
C(102)-C(107)-C(108)	110.8(2)
C(107)-C(108)-C(109)	104.1(2)
C(107)-C(108)-H(10A)	110.9
C(109)-C(108)-H(10A)	110.9
C(107)-C(108)-H(10B)	110.9
C(109)-C(108)-H(10B)	110.9
H(10A)-C(108)-H(10B)	109.0

N(101)-C(109)-C(108)	106.2(2)
N(101)-C(109)-H(10C)	110.5
C(108)-C(109)-H(10C)	110.5
N(101)-C(109)-H(10D)	110.5
C(108)-C(109)-H(10D)	110.5
H(10C)-C(109)-H(10D)	108.7
N(102)-C(110)-C(120)	109.33(17)
N(102)-C(110)-C(101)	109.60(17)
C(120)-C(110)-C(101)	110.19(18)
N(102)-C(110)-C(126)	108.88(17)
C(120)-C(110)-C(126)	108.77(17)
C(101)-C(110)-C(126)	110.04(18)
C(111)-N(102)-C(118)	107.48(18)
C(111)-N(102)-C(110)	125.74(18)
C(118)-N(102)-C(110)	124.98(18)
N(102)-C(111)-C(112)	130.8(2)
N(102)-C(111)-C(116)	107.72(19)
C(112)-C(111)-C(116)	121.5(2)
C(113)-C(112)-C(111)	117.7(2)
C(113)-C(112)-H(112)	121.1
C(111)-C(112)-H(112)	121.1
C(112)-C(113)-C(114)	119.9(2)
C(112)-C(113)-H(113)	120.1
C(114)-C(113)-H(113)	120.1
F(101)-C(114)-C(115)	118.6(2)
F(101)-C(114)-C(113)	117.2(2)
C(115)-C(114)-C(113)	124.2(2)
C(114)-C(115)-C(116)	117.0(2)
C(114)-C(115)-H(115)	121.5
C(116)-C(115)-H(115)	121.5
C(115)-C(116)-C(111)	119.8(2)
C(115)-C(116)-C(117)	133.1(2)
C(111)-C(116)-C(117)	107.17(19)
C(118)-C(117)-C(116)	106.7(2)
C(118)-C(117)-C(119)	126.4(2)
C(116)-C(117)-C(119)	126.9(2)
C(117)-C(118)-N(102)	110.9(2)
C(117)-C(118)-H(118)	124.6
N(102)-C(118)-H(118)	124.6
C(117)-C(119)-H(11A)	109.5
C(117)-C(119)-H(11B)	109.5
H(11A)-C(119)-H(11B)	109.5
C(117)-C(119)-H(11C)	109.5

H(11A)-C(119)-H(11C)	109.5
H(11B)-C(119)-H(11C)	109.5
C(121)-C(120)-C(125)	117.9(2)
C(121)-C(120)-C(110)	120.73(19)
C(125)-C(120)-C(110)	121.2(2)
C(120)-C(121)-C(122)	121.1(2)
C(120)-C(121)-H(121)	119.5
C(122)-C(121)-H(121)	119.5
C(123)-C(122)-C(121)	120.3(2)
C(123)-C(122)-H(122)	119.8
C(121)-C(122)-H(122)	119.8
C(122)-C(123)-C(124)	119.4(2)
C(122)-C(123)-H(123)	120.3
C(124)-C(123)-H(123)	120.3
C(123)-C(124)-C(125)	120.5(2)
C(123)-C(124)-H(124)	119.8
C(125)-C(124)-H(124)	119.8
C(124)-C(125)-C(120)	120.8(2)
C(124)-C(125)-H(125)	119.6
C(120)-C(125)-H(125)	119.6
C(127)-C(126)-C(110)	116.00(18)
C(127)-C(126)-H(12A)	108.3
C(110)-C(126)-H(12A)	108.3
C(127)-C(126)-H(12B)	108.3
C(110)-C(126)-H(12B)	108.3
H(12A)-C(126)-H(12B)	107.4
C(126)-C(127)-H(12C)	109.5
C(126)-C(127)-H(12D)	109.5
H(12C)-C(127)-H(12D)	109.5
C(126)-C(127)-H(12E)	109.5
H(12C)-C(127)-H(12E)	109.5
H(12D)-C(127)-H(12E)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,z

Table S20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for P15247. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(1)	17(1)	18(1)	-4(1)	1(1)	3(1)
C(1)	16(1)	14(1)	13(1)	2(1)	5(1)	0(1)
N(1)	13(1)	13(1)	15(1)	-1(1)	3(1)	0(1)
C(2)	14(1)	18(1)	11(1)	5(1)	4(1)	1(1)
C(3)	17(1)	19(1)	16(1)	0(1)	6(1)	1(1)
C(4)	19(1)	26(1)	15(1)	-2(1)	1(1)	0(1)
C(5)	20(1)	29(1)	20(1)	2(1)	-2(1)	5(1)
C(6)	19(1)	23(1)	25(1)	3(1)	4(1)	5(1)
C(7)	16(1)	19(1)	17(1)	3(1)	6(1)	2(1)
C(8)	20(1)	16(1)	22(1)	1(1)	4(1)	4(1)
C(9)	16(1)	15(1)	19(1)	-3(1)	4(1)	2(1)
C(10)	15(1)	12(1)	13(1)	-1(1)	4(1)	1(1)
N(2)	15(1)	13(1)	12(1)	-1(1)	3(1)	-1(1)
C(11)	12(1)	16(1)	14(1)	4(1)	3(1)	3(1)
C(12)	17(1)	17(1)	18(1)	1(1)	3(1)	0(1)
C(13)	16(1)	20(1)	28(1)	7(1)	5(1)	1(1)
C(14)	21(1)	27(1)	24(1)	11(1)	14(1)	5(1)
F(1)	36(1)	35(1)	40(1)	12(1)	27(1)	1(1)
C(15)	21(1)	25(1)	17(1)	4(1)	9(1)	7(1)
C(16)	15(1)	19(1)	13(1)	3(1)	2(1)	5(1)
C(17)	18(1)	18(1)	14(1)	0(1)	2(1)	4(1)
C(19)	26(1)	25(1)	17(1)	-4(1)	3(1)	3(1)
C(18)	14(1)	15(1)	15(1)	0(1)	1(1)	0(1)
C(20)	17(1)	12(1)	17(1)	0(1)	7(1)	2(1)
C(21)	16(1)	17(1)	19(1)	-1(1)	6(1)	0(1)
C(22)	20(1)	20(1)	29(1)	-3(1)	12(1)	-2(1)
C(23)	28(1)	18(1)	36(1)	5(1)	20(1)	2(1)
C(24)	29(1)	24(1)	24(1)	9(1)	13(1)	8(1)
C(25)	18(1)	21(1)	20(1)	3(1)	8(1)	5(1)
C(26)	17(1)	12(1)	17(1)	0(1)	3(1)	2(1)
C(27)	20(1)	15(1)	22(1)	1(1)	-2(1)	2(1)
O(101)	17(1)	19(1)	24(1)	9(1)	-1(1)	-2(1)
C(101)	15(1)	14(1)	13(1)	0(1)	5(1)	1(1)
N(101)	12(1)	15(1)	17(1)	4(1)	2(1)	-1(1)
C(102)	13(1)	21(1)	14(1)	-2(1)	4(1)	1(1)
C(103)	18(1)	26(1)	15(1)	1(1)	4(1)	1(1)
C(104)	21(1)	34(1)	17(1)	2(1)	0(1)	5(1)
C(105)	18(1)	48(2)	21(1)	-6(1)	-2(1)	3(1)

C(106)	15(1)	36(2)	28(1)	-10(1)	4(1)	-5(1)
C(107)	17(1)	22(1)	20(1)	-6(1)	7(1)	-1(1)
C(108)	21(1)	21(1)	26(1)	-2(1)	7(1)	-5(1)
C(109)	22(1)	29(2)	44(2)	19(1)	-3(1)	-10(1)
C(110)	15(1)	14(1)	13(1)	2(1)	4(1)	2(1)
N(102)	16(1)	13(1)	13(1)	2(1)	4(1)	1(1)
C(111)	14(1)	13(1)	16(1)	-1(1)	4(1)	-3(1)
C(112)	18(1)	14(1)	18(1)	1(1)	6(1)	-2(1)
C(113)	17(1)	15(1)	26(1)	-2(1)	6(1)	-1(1)
C(114)	18(1)	22(1)	23(1)	-11(1)	8(1)	-4(1)
F(101)	32(1)	32(1)	32(1)	-10(1)	18(1)	3(1)
C(115)	20(1)	26(1)	15(1)	-1(1)	6(1)	-6(1)
C(116)	15(1)	18(1)	14(1)	-1(1)	2(1)	-5(1)
C(117)	19(1)	17(1)	15(1)	1(1)	3(1)	-5(1)
C(118)	17(1)	14(1)	17(1)	3(1)	2(1)	-1(1)
C(119)	30(1)	24(1)	16(1)	6(1)	6(1)	-1(1)
C(120)	12(1)	13(1)	18(1)	2(1)	2(1)	3(1)
C(121)	17(1)	18(1)	18(1)	3(1)	3(1)	2(1)
C(122)	20(1)	22(1)	21(1)	1(1)	-1(1)	-1(1)
C(123)	14(1)	20(1)	31(1)	2(1)	3(1)	-1(1)
C(124)	16(1)	19(1)	27(1)	4(1)	8(1)	1(1)
C(125)	17(1)	16(1)	20(1)	1(1)	6(1)	1(1)
C(126)	17(1)	15(1)	17(1)	1(1)	4(1)	2(1)
C(127)	25(1)	19(1)	19(1)	-1(1)	8(1)	2(1)

Table S21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for P15247.

	x	y	z	U(eq)
H(3)	4312	3349	3314	20
H(4)	4876	2875	4280	25
H(5)	5256	-179	4354	29
H(6)	5079	-2821	3454	27
H(8A)	4368	-4224	2419	23
H(8B)	4599	-2981	1928	23
H(9A)	4040	-1469	1308	20
H(9B)	3815	-2589	1835	20
H(12)	3887	4199	1065	21
H(13)	4263	5318	298	26
H(15)	3909	249	-1041	24
H(19A)	3233	-4395	-601	35
H(19B)	3549	-3408	-961	35
H(19C)	3111	-2555	-1200	35
H(18)	3119	-2318	526	18
H(21)	2645	-617	931	21
H(22)	2283	-2850	1472	27
H(23)	2535	-3985	2677	30
H(24)	3150	-2831	3335	29
H(25)	3511	-572	2806	23
H(26A)	3023	3762	1742	19
H(26B)	3301	4541	1267	19
H(27A)	2849	2713	237	31
H(27B)	2697	4887	502	31
H(27C)	2557	2642	737	31
H(103)	4327	6971	8390	24
H(104)	4905	6678	9336	30
H(105)	5388	9249	9500	36
H(106)	5314	12122	8693	32
H(10A)	4830	12854	7150	27
H(10B)	4693	14395	7707	27
H(10C)	4074	13583	7206	41
H(10D)	4208	12366	6574	41
H(112)	3999	6669	6378	20
H(113)	4331	4798	5665	23
H(115)	4041	9244	4064	24
H(118)	3299	13222	5463	20

H(11A)	3330	12330	3729	35
H(11B)	3743	13471	4015	35
H(11C)	3373	14429	4221	35
H(121)	3098	8265	5335	21
H(122)	2549	6077	5041	26
H(123)	2249	5097	5932	27
H(124)	2510	6241	7131	24
H(125)	3064	8367	7435	21
H(12A)	3475	13520	6669	20
H(12B)	3054	12522	6562	20
H(12C)	3251	11399	7813	31
H(12D)	3247	13937	7722	31
H(12E)	3649	12666	7903	31

Table S22. Torsion angles [°] for P15247.

O(1)-C(1)-N(1)-C(2)	10.0(3)
C(10)-C(1)-N(1)-C(2)	-166.92(18)
O(1)-C(1)-N(1)-C(9)	178.5(2)
C(10)-C(1)-N(1)-C(9)	1.6(3)
C(1)-N(1)-C(2)-C(3)	-6.5(3)
C(9)-N(1)-C(2)-C(3)	-176.7(2)
C(1)-N(1)-C(2)-C(7)	171.21(19)
C(9)-N(1)-C(2)-C(7)	1.0(2)
C(7)-C(2)-C(3)-C(4)	0.1(3)
N(1)-C(2)-C(3)-C(4)	177.5(2)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(3)-C(4)-C(5)-C(6)	0.0(4)
C(4)-C(5)-C(6)-C(7)	-0.5(4)
C(5)-C(6)-C(7)-C(2)	0.7(3)
C(5)-C(6)-C(7)-C(8)	-179.2(2)
C(3)-C(2)-C(7)-C(6)	-0.5(3)
N(1)-C(2)-C(7)-C(6)	-178.45(19)
C(3)-C(2)-C(7)-C(8)	179.4(2)
N(1)-C(2)-C(7)-C(8)	1.5(2)
C(6)-C(7)-C(8)-C(9)	176.7(2)
C(2)-C(7)-C(8)-C(9)	-3.2(2)
C(1)-N(1)-C(9)-C(8)	-172.76(19)
C(2)-N(1)-C(9)-C(8)	-2.9(2)
C(7)-C(8)-C(9)-N(1)	3.6(2)
O(1)-C(1)-C(10)-N(2)	136.1(2)
N(1)-C(1)-C(10)-N(2)	-46.9(3)
O(1)-C(1)-C(10)-C(20)	-99.9(2)
N(1)-C(1)-C(10)-C(20)	77.1(2)
O(1)-C(1)-C(10)-C(26)	18.1(3)
N(1)-C(1)-C(10)-C(26)	-164.90(18)
C(20)-C(10)-N(2)-C(18)	9.1(3)
C(26)-C(10)-N(2)-C(18)	-113.4(2)
C(1)-C(10)-N(2)-C(18)	130.3(2)
C(20)-C(10)-N(2)-C(11)	-172.47(19)
C(26)-C(10)-N(2)-C(11)	65.1(2)
C(1)-C(10)-N(2)-C(11)	-51.3(3)
C(18)-N(2)-C(11)-C(12)	-177.9(2)
C(10)-N(2)-C(11)-C(12)	3.3(4)
C(18)-N(2)-C(11)-C(16)	-0.2(2)
C(10)-N(2)-C(11)-C(16)	-178.97(19)
N(2)-C(11)-C(12)-C(13)	177.7(2)

C(16)-C(11)-C(12)-C(13)	0.3(3)
C(11)-C(12)-C(13)-C(14)	-0.6(3)
C(12)-C(13)-C(14)-C(15)	0.2(4)
C(12)-C(13)-C(14)-F(1)	-179.7(2)
F(1)-C(14)-C(15)-C(16)	-179.5(2)
C(13)-C(14)-C(15)-C(16)	0.6(4)
C(14)-C(15)-C(16)-C(11)	-0.9(3)
C(14)-C(15)-C(16)-C(17)	-179.0(2)
N(2)-C(11)-C(16)-C(15)	-177.4(2)
C(12)-C(11)-C(16)-C(15)	0.5(3)
N(2)-C(11)-C(16)-C(17)	1.0(2)
C(12)-C(11)-C(16)-C(17)	179.0(2)
C(15)-C(16)-C(17)-C(18)	176.8(2)
C(11)-C(16)-C(17)-C(18)	-1.4(2)
C(15)-C(16)-C(17)-C(19)	-4.7(4)
C(11)-C(16)-C(17)-C(19)	177.1(2)
C(16)-C(17)-C(18)-N(2)	1.3(3)
C(19)-C(17)-C(18)-N(2)	-177.2(2)
C(11)-N(2)-C(18)-C(17)	-0.7(2)
C(10)-N(2)-C(18)-C(17)	178.0(2)
N(2)-C(10)-C(20)-C(25)	125.1(2)
C(26)-C(10)-C(20)-C(25)	-113.0(2)
C(1)-C(10)-C(20)-C(25)	2.6(3)
N(2)-C(10)-C(20)-C(21)	-60.6(3)
C(26)-C(10)-C(20)-C(21)	61.3(3)
C(1)-C(10)-C(20)-C(21)	176.97(19)
C(25)-C(20)-C(21)-C(22)	-0.3(3)
C(10)-C(20)-C(21)-C(22)	-174.9(2)
C(20)-C(21)-C(22)-C(23)	-0.2(4)
C(21)-C(22)-C(23)-C(24)	0.4(4)
C(22)-C(23)-C(24)-C(25)	0.0(4)
C(23)-C(24)-C(25)-C(20)	-0.6(4)
C(21)-C(20)-C(25)-C(24)	0.7(3)
C(10)-C(20)-C(25)-C(24)	175.3(2)
N(2)-C(10)-C(26)-C(27)	47.5(2)
C(20)-C(10)-C(26)-C(27)	-76.8(2)
C(1)-C(10)-C(26)-C(27)	166.34(18)
O(101)-C(101)-N(101)-C(102)	-3.4(3)
C(110)-C(101)-N(101)-C(102)	176.19(19)
O(101)-C(101)-N(101)-C(109)	-175.0(2)
C(110)-C(101)-N(101)-C(109)	4.6(3)
C(101)-N(101)-C(102)-C(103)	2.8(4)
C(109)-N(101)-C(102)-C(103)	175.8(2)

C(101)-N(101)-C(102)-C(107)	-175.93(19)
C(109)-N(101)-C(102)-C(107)	-2.9(3)
C(107)-C(102)-C(103)-C(104)	1.6(3)
N(101)-C(102)-C(103)-C(104)	-177.0(2)
C(102)-C(103)-C(104)-C(105)	0.1(4)
C(103)-C(104)-C(105)-C(106)	-1.4(4)
C(104)-C(105)-C(106)-C(107)	0.9(4)
C(105)-C(106)-C(107)-C(102)	0.8(3)
C(105)-C(106)-C(107)-C(108)	-179.5(2)
C(103)-C(102)-C(107)-C(106)	-2.1(3)
N(101)-C(102)-C(107)-C(106)	176.8(2)
C(103)-C(102)-C(107)-C(108)	178.2(2)
N(101)-C(102)-C(107)-C(108)	-3.0(3)
C(106)-C(107)-C(108)-C(109)	-172.3(3)
C(102)-C(107)-C(108)-C(109)	7.4(3)
C(101)-N(101)-C(109)-C(108)	-179.8(2)
C(102)-N(101)-C(109)-C(108)	7.5(3)
C(107)-C(108)-C(109)-N(101)	-8.8(3)
O(101)-C(101)-C(110)-N(102)	-127.1(2)
N(101)-C(101)-C(110)-N(102)	53.3(3)
O(101)-C(101)-C(110)-C(120)	-6.8(3)
N(101)-C(101)-C(110)-C(120)	173.66(18)
O(101)-C(101)-C(110)-C(126)	113.2(2)
N(101)-C(101)-C(110)-C(126)	-66.4(2)
C(120)-C(110)-N(102)-C(111)	-73.7(3)
C(101)-C(110)-N(102)-C(111)	47.2(3)
C(126)-C(110)-N(102)-C(111)	167.58(19)
C(120)-C(110)-N(102)-C(118)	89.1(2)
C(101)-C(110)-N(102)-C(118)	-150.0(2)
C(126)-C(110)-N(102)-C(118)	-29.6(3)
C(118)-N(102)-C(111)-C(112)	-175.7(2)
C(110)-N(102)-C(111)-C(112)	-10.4(4)
C(118)-N(102)-C(111)-C(116)	3.2(2)
C(110)-N(102)-C(111)-C(116)	168.50(19)
N(102)-C(111)-C(112)-C(113)	-179.3(2)
C(116)-C(111)-C(112)-C(113)	1.9(3)
C(111)-C(112)-C(113)-C(114)	0.6(3)
C(112)-C(113)-C(114)-F(101)	178.7(2)
C(112)-C(113)-C(114)-C(115)	-2.1(4)
F(101)-C(114)-C(115)-C(116)	-179.9(2)
C(113)-C(114)-C(115)-C(116)	1.0(4)
C(114)-C(115)-C(116)-C(111)	1.6(3)
C(114)-C(115)-C(116)-C(117)	-178.1(2)

N(102)-C(111)-C(116)-C(115)	177.9(2)
C(112)-C(111)-C(116)-C(115)	-3.1(3)
N(102)-C(111)-C(116)-C(117)	-2.4(2)
C(112)-C(111)-C(116)-C(117)	176.6(2)
C(115)-C(116)-C(117)-C(118)	-179.7(2)
C(111)-C(116)-C(117)-C(118)	0.6(2)
C(115)-C(116)-C(117)-C(119)	0.6(4)
C(111)-C(116)-C(117)-C(119)	-179.1(2)
C(116)-C(117)-C(118)-N(102)	1.4(3)
C(119)-C(117)-C(118)-N(102)	-178.9(2)
C(111)-N(102)-C(118)-C(117)	-2.9(3)
C(110)-N(102)-C(118)-C(117)	-168.4(2)
N(102)-C(110)-C(120)-C(121)	-5.7(3)
C(101)-C(110)-C(120)-C(121)	-126.2(2)
C(126)-C(110)-C(120)-C(121)	113.1(2)
N(102)-C(110)-C(120)-C(125)	178.9(2)
C(101)-C(110)-C(120)-C(125)	58.4(3)
C(126)-C(110)-C(120)-C(125)	-62.3(3)
C(125)-C(120)-C(121)-C(122)	1.0(3)
C(110)-C(120)-C(121)-C(122)	-174.6(2)
C(120)-C(121)-C(122)-C(123)	0.4(4)
C(121)-C(122)-C(123)-C(124)	-1.0(4)
C(122)-C(123)-C(124)-C(125)	0.3(4)
C(123)-C(124)-C(125)-C(120)	1.0(4)
C(121)-C(120)-C(125)-C(124)	-1.6(3)
C(110)-C(120)-C(125)-C(124)	173.9(2)
N(102)-C(110)-C(126)-C(127)	-150.58(19)
C(120)-C(110)-C(126)-C(127)	90.4(2)
C(101)-C(110)-C(126)-C(127)	-30.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,z

VII. References

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VIII. ^{1}H, ^{13}C, and ^{31}P NMR Spectral Data

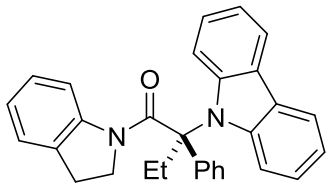


Table 1B, Entry 1
($CDCl_3$, 500 MHz)

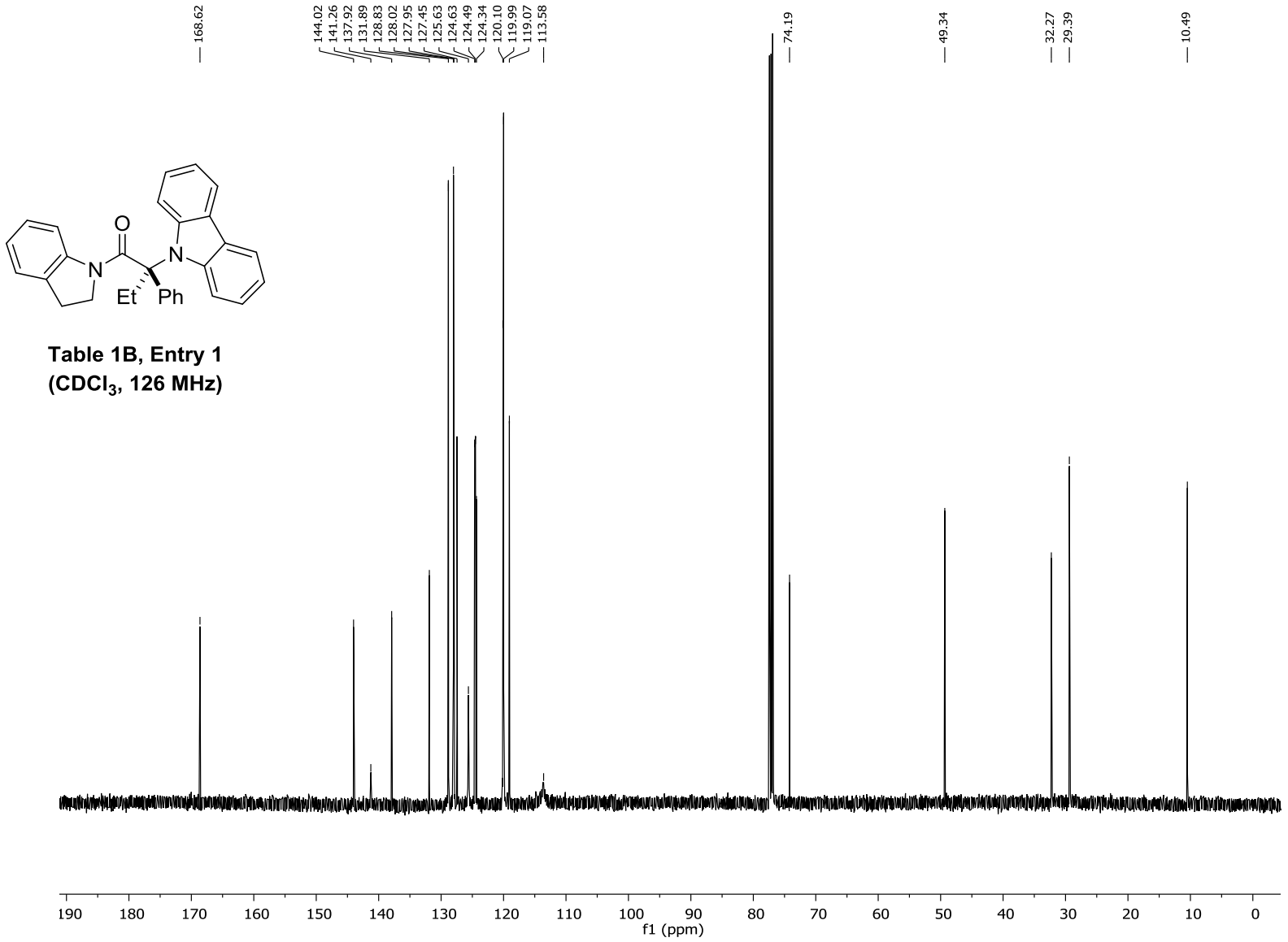


Table 1B, Entry 1
($CDCl_3$, 126 MHz)

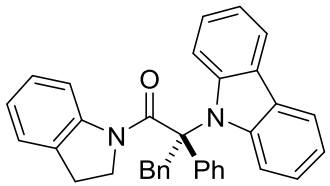
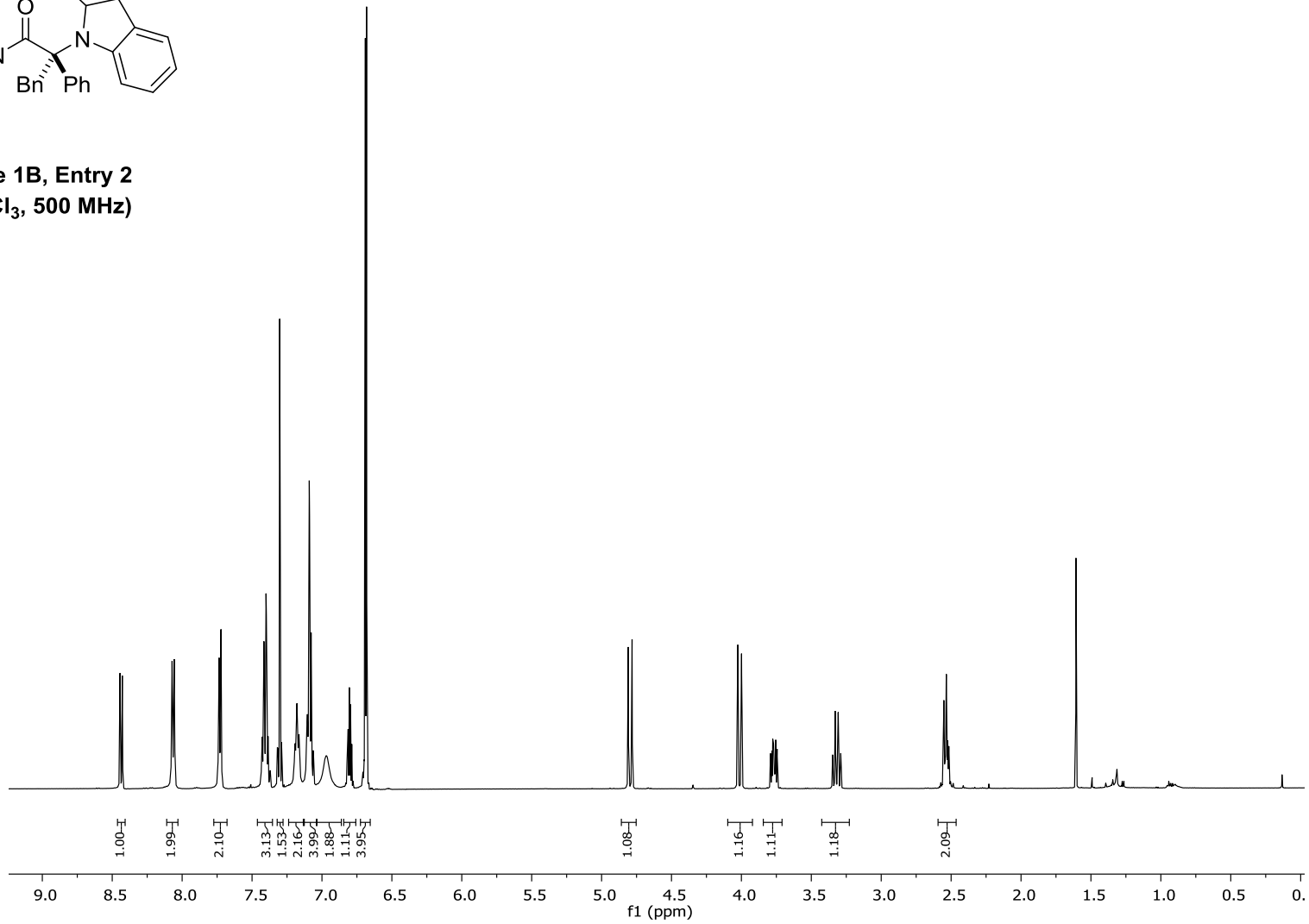


Table 1B, Entry 2
($CDCl_3$, 500 MHz)



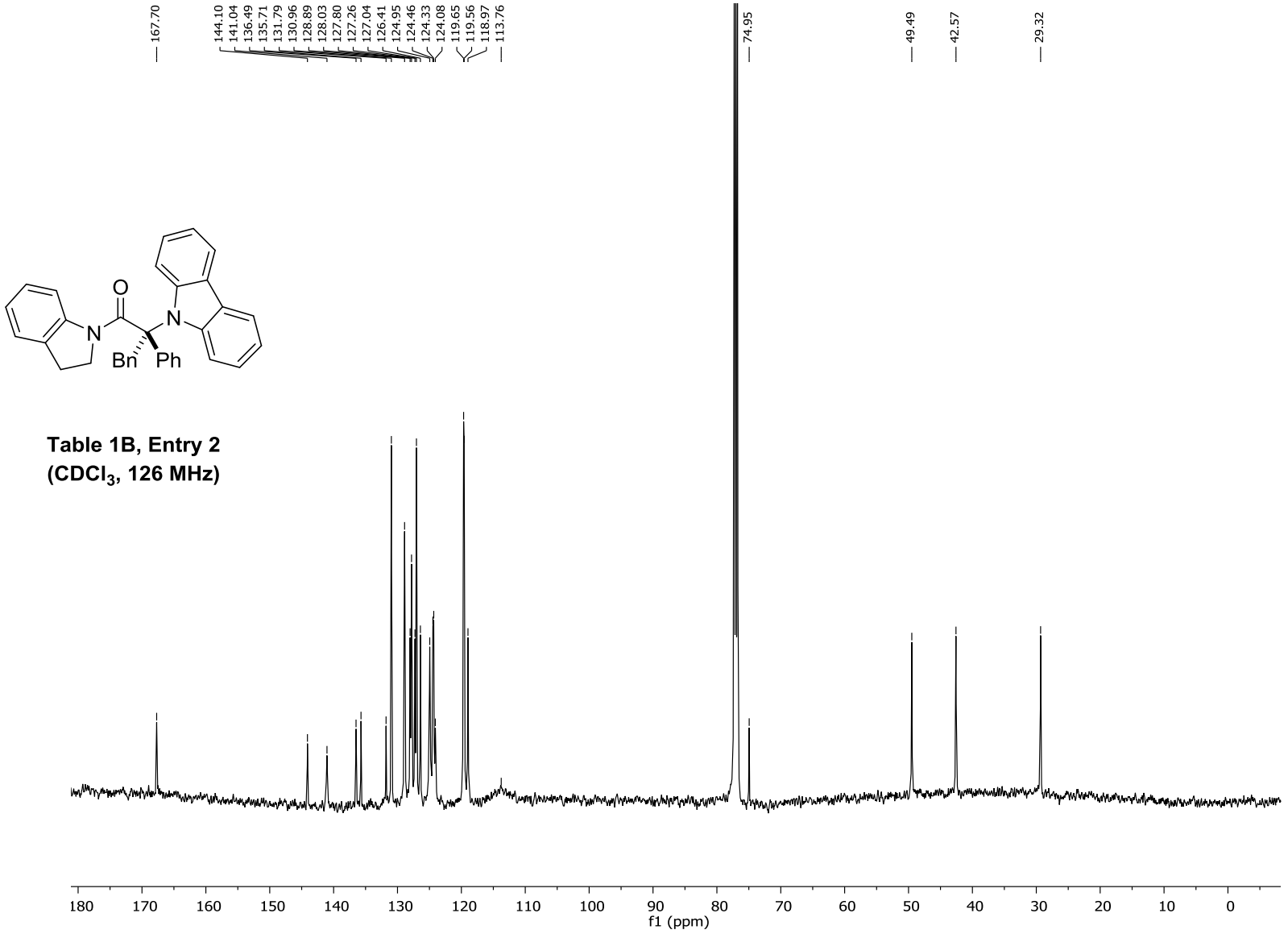


Table 1B, Entry 2
($CDCl_3$, 126 MHz)

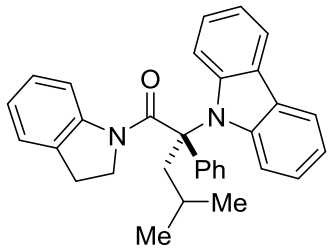


Table 1B, Entry 3
($CDCl_3$, 500 MHz)

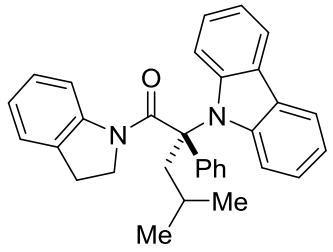


Table 1B, Entry 3
($CDCl_3$, 126 MHz)

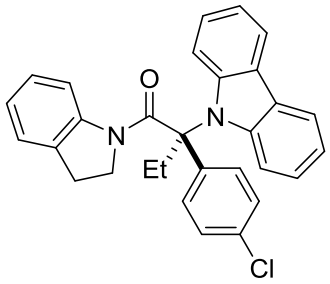
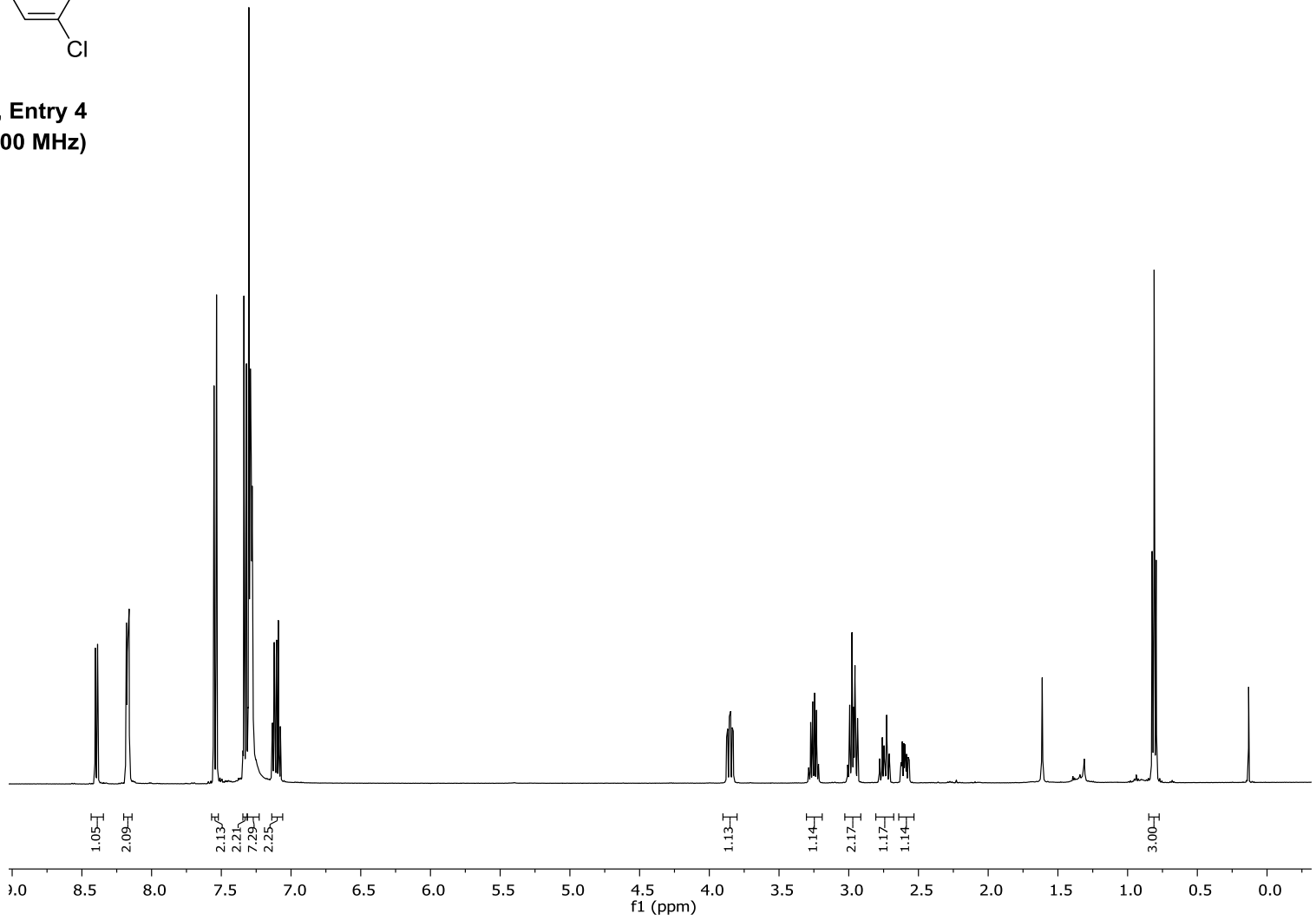


Table 1B, Entry 4
($CDCl_3$, 500 MHz)



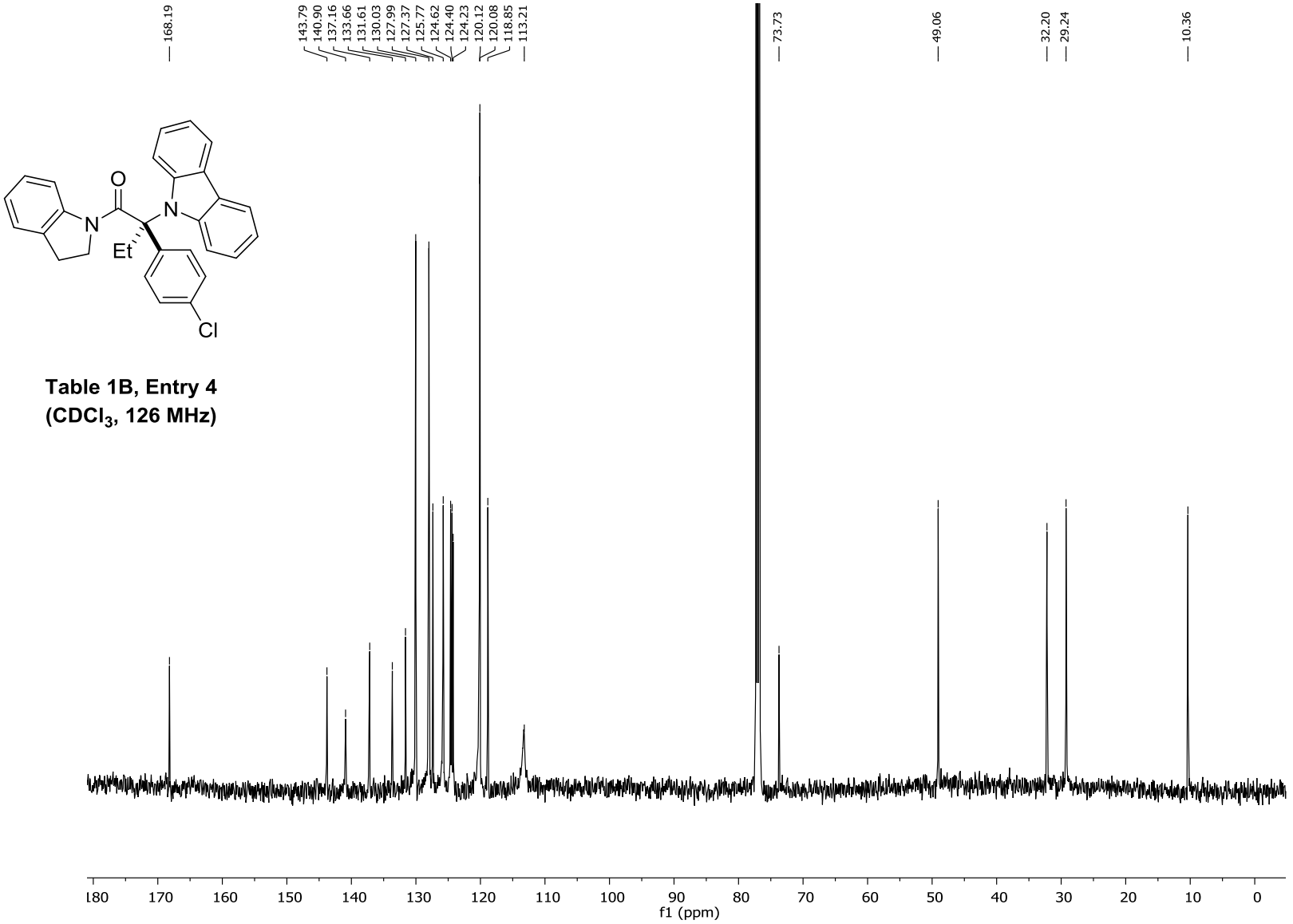


Table 1B, Entry 4
($CDCl_3$, 126 MHz)

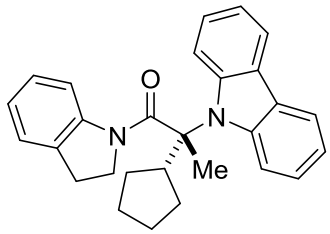
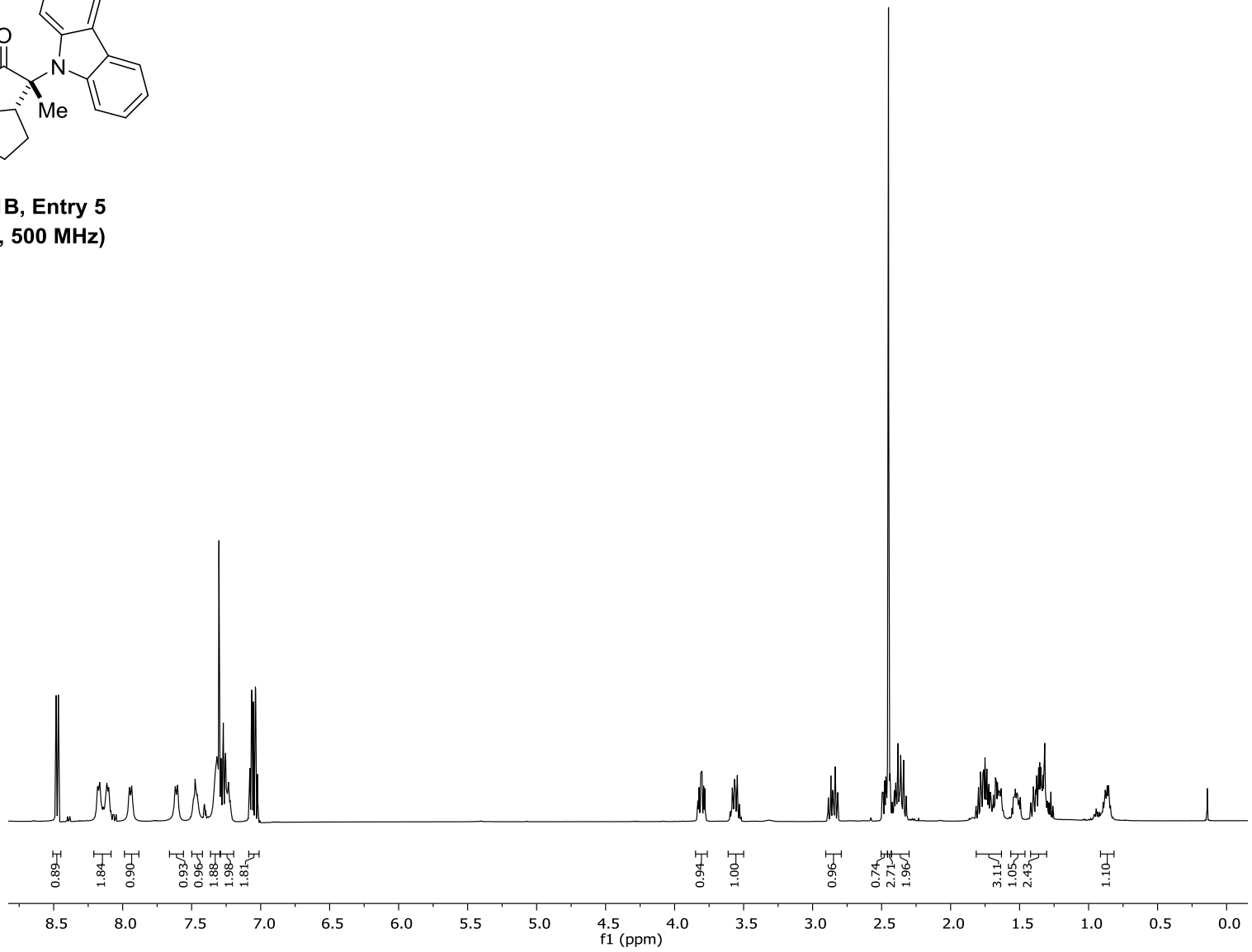


Table 1B, Entry 5
($CDCl_3$, 500 MHz)



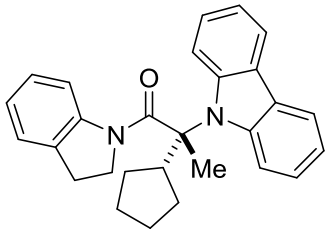


Table 1B, Entry 5
($CDCl_3$, 126 MHz)

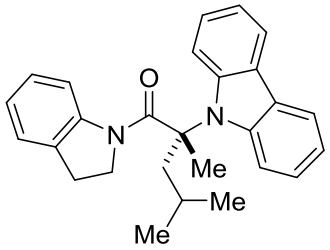


Table 1B, Entry 6
($CDCl_3$, 500 MHz)

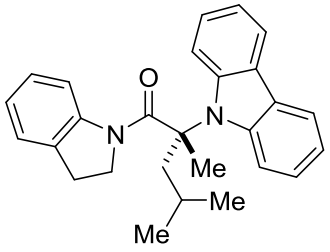
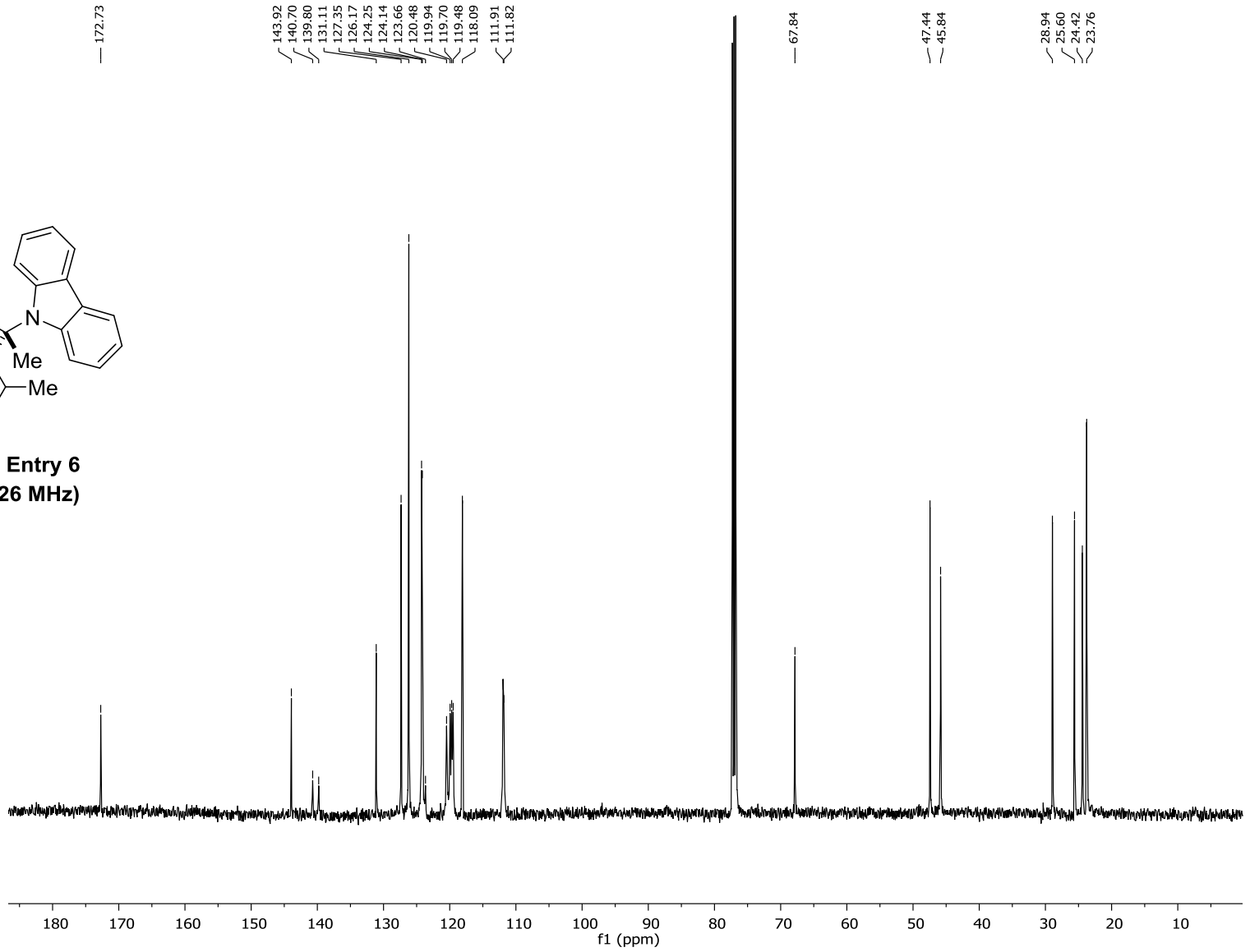


Table 1B, Entry 6
($CDCl_3$, 126 MHz)



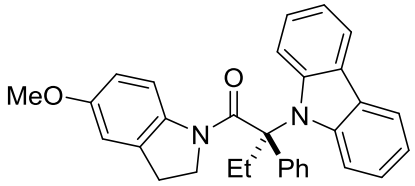


Table 1B, Entry 7
($CDCl_3$, 500 MHz)

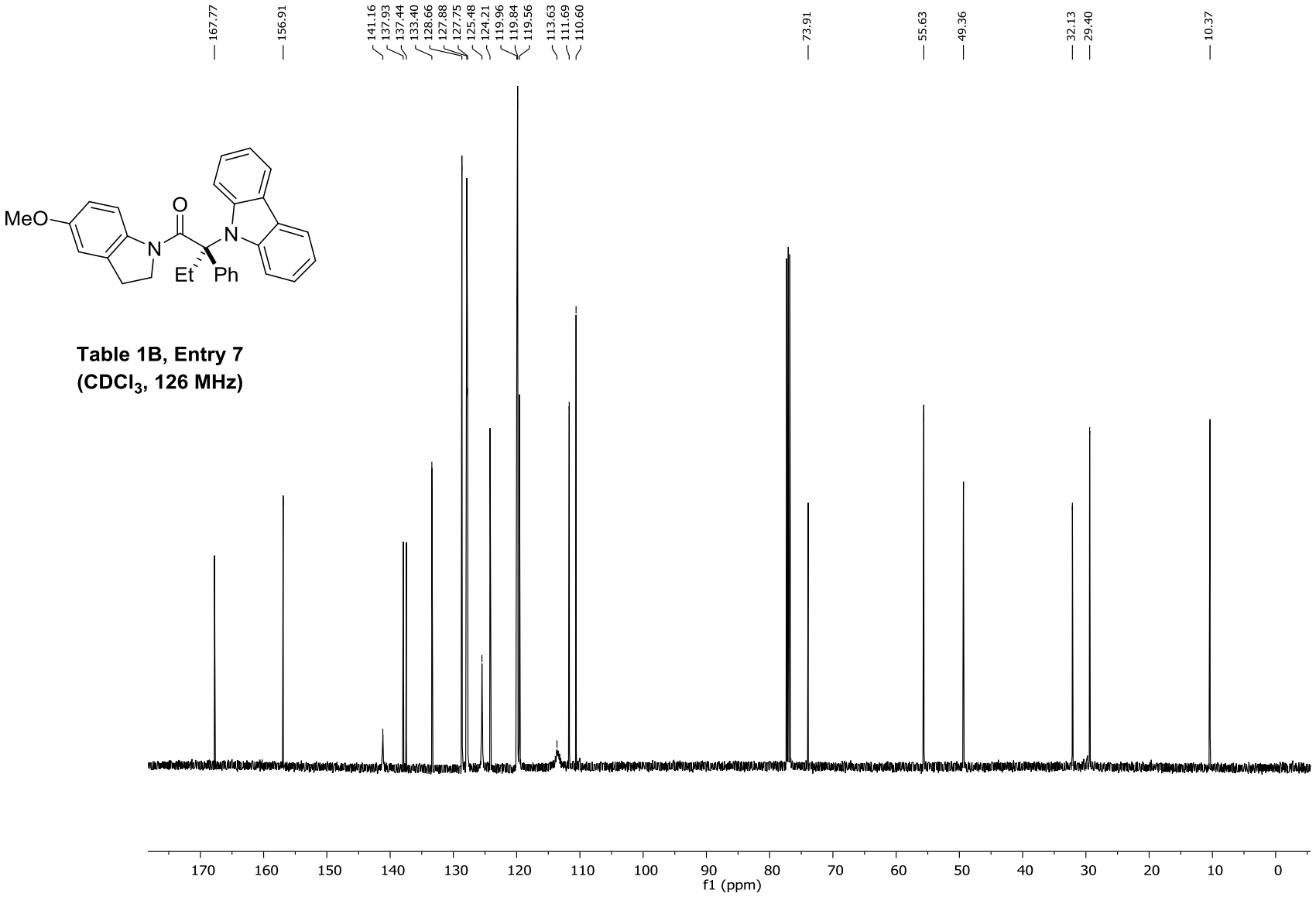


Table 1B, Entry 7
($CDCl_3$, 126 MHz)

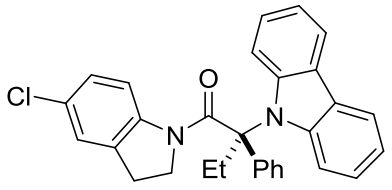
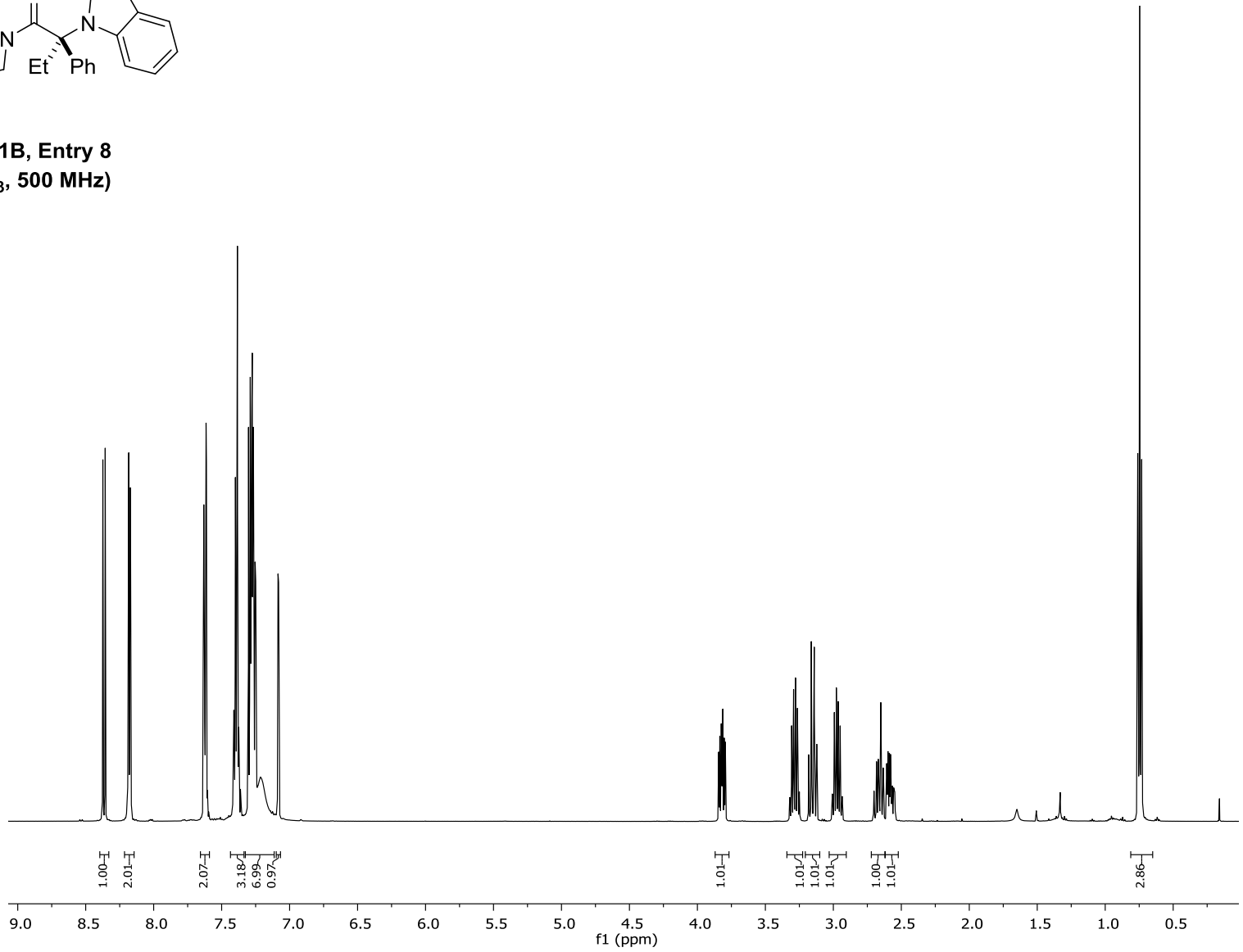


Table 1B, Entry 8
($CDCl_3$, 500 MHz)



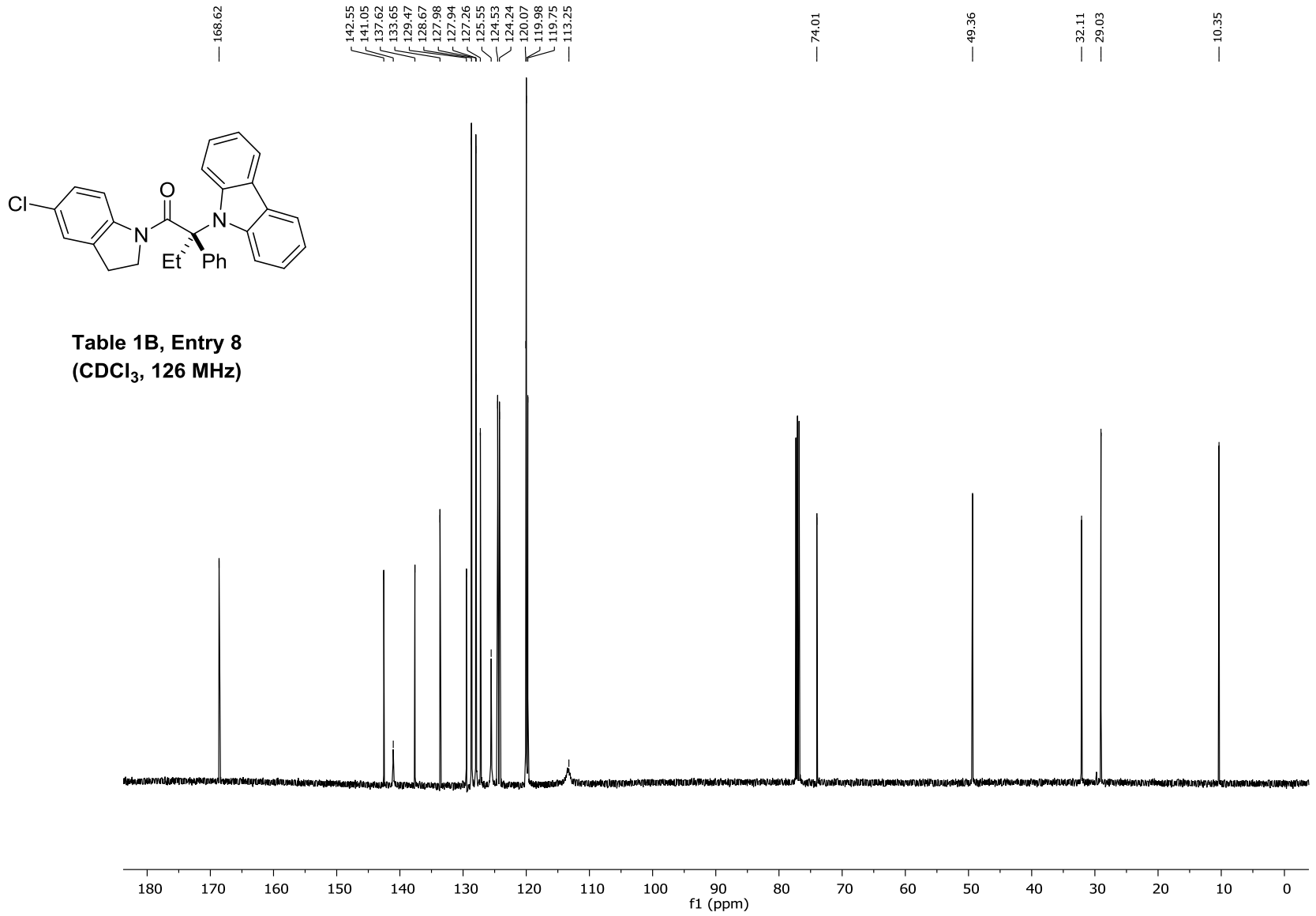


Table 1B, Entry 8
($CDCl_3$, 126 MHz)

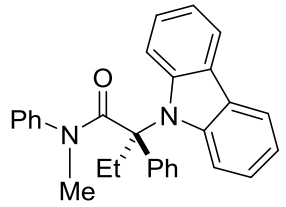


Table 1B, Entry 9
(d_6-DMSO, 500 MHz, 80 °C)

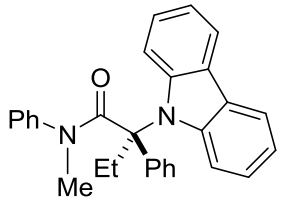


Table 1B, Entry 9
(d_6-DMSO, 500 MHz, 80 °C)

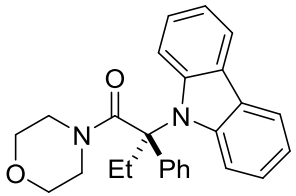


Table 1B, Entry 10
(d_6-DMSO, 500 MHz, 80 °C)

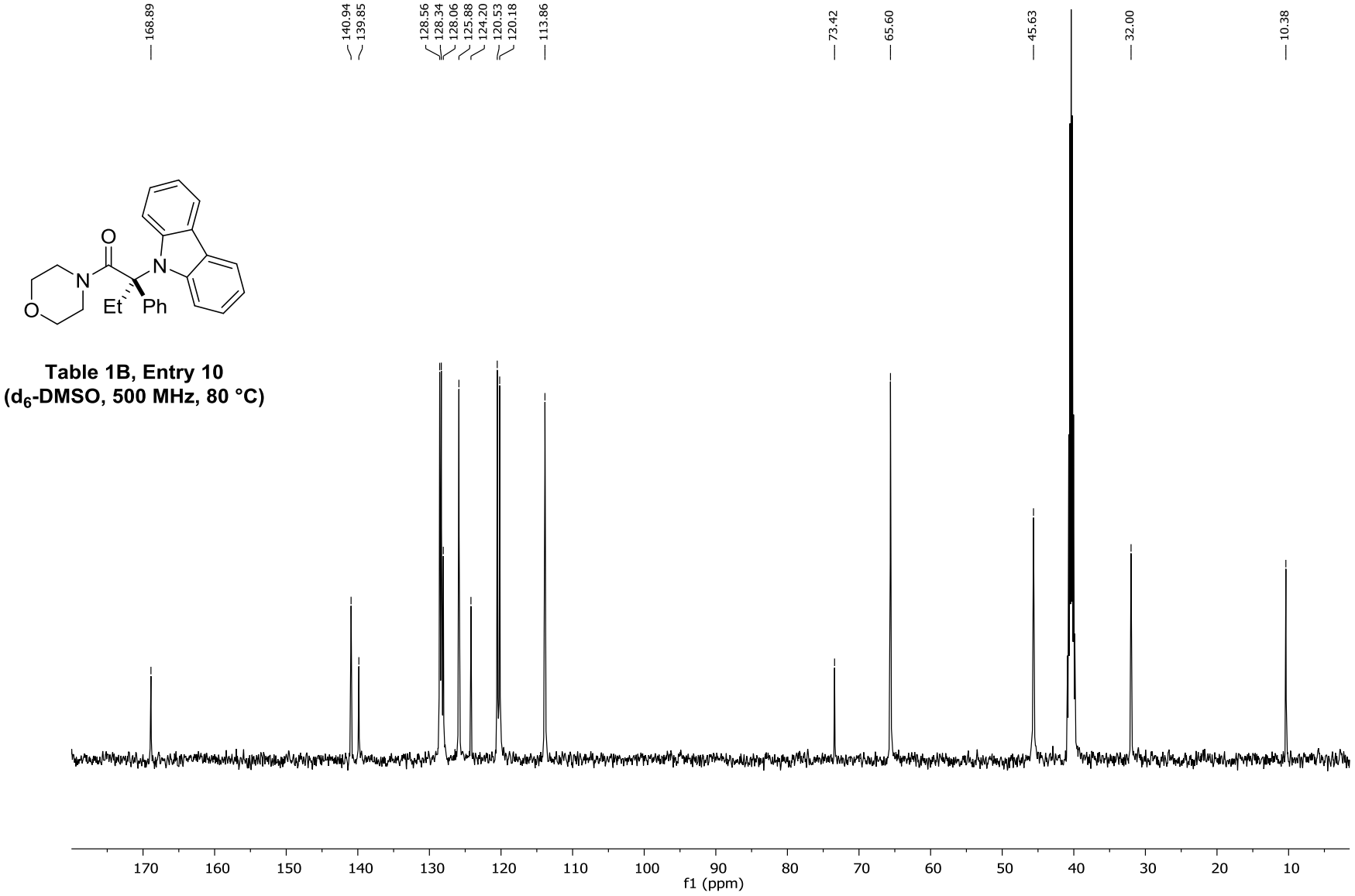


Table 1B, Entry 10
(d_6-DMSO, 500 MHz, 80 °C)

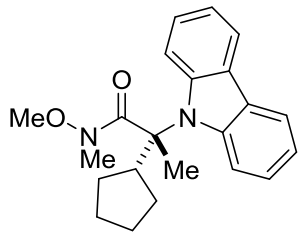


Table 1B, Entry 11
(d_6-DMSO, 500 MHz, 80 °C)

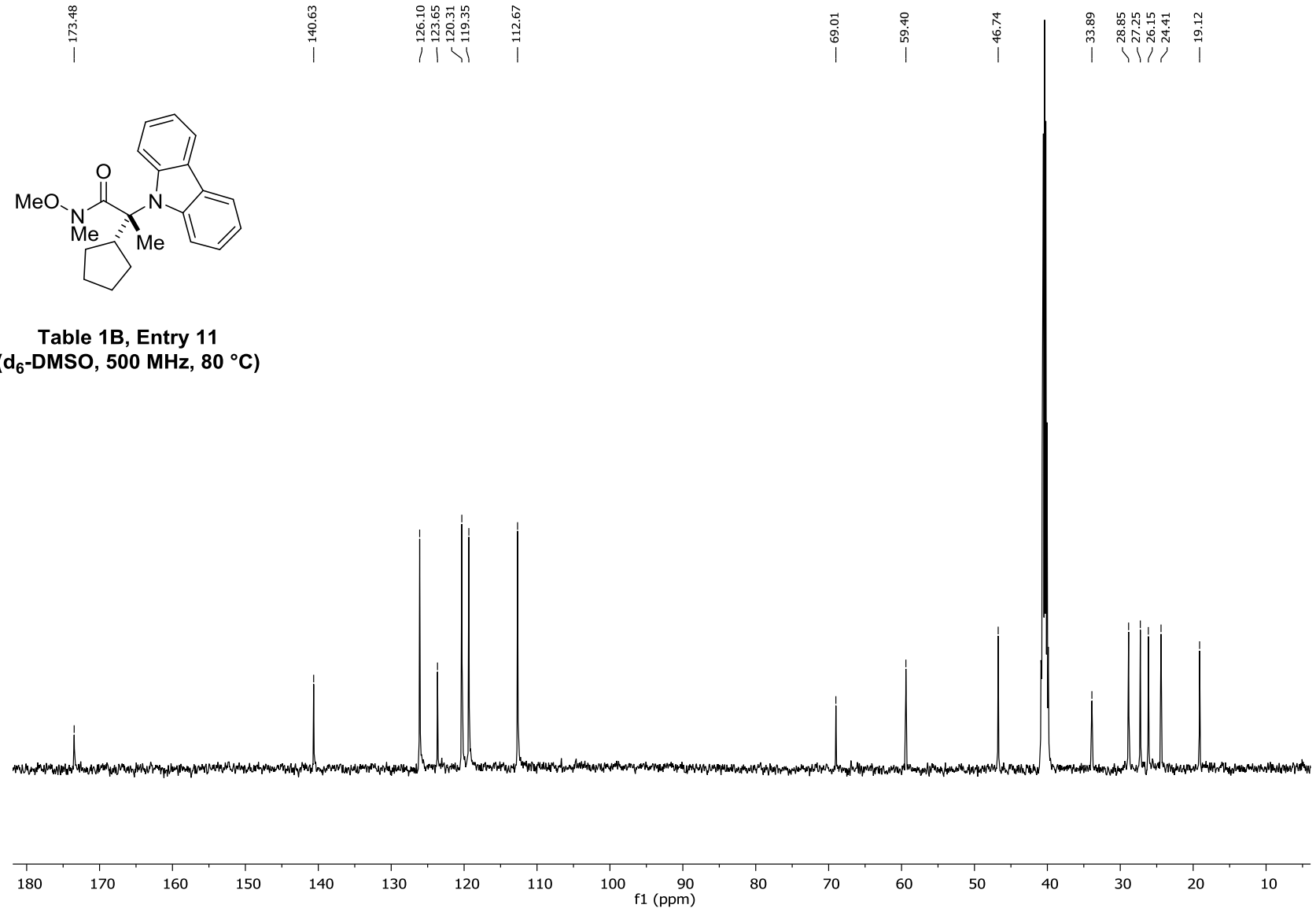


Table 1B, Entry 11
(d_6-DMSO, 500 MHz, 80 °C)

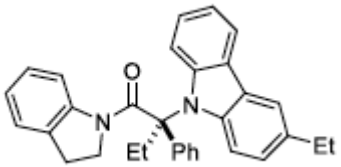


Table 1C, Entry 1
(d_6-DMSO, 500 MHz, 80 °C)

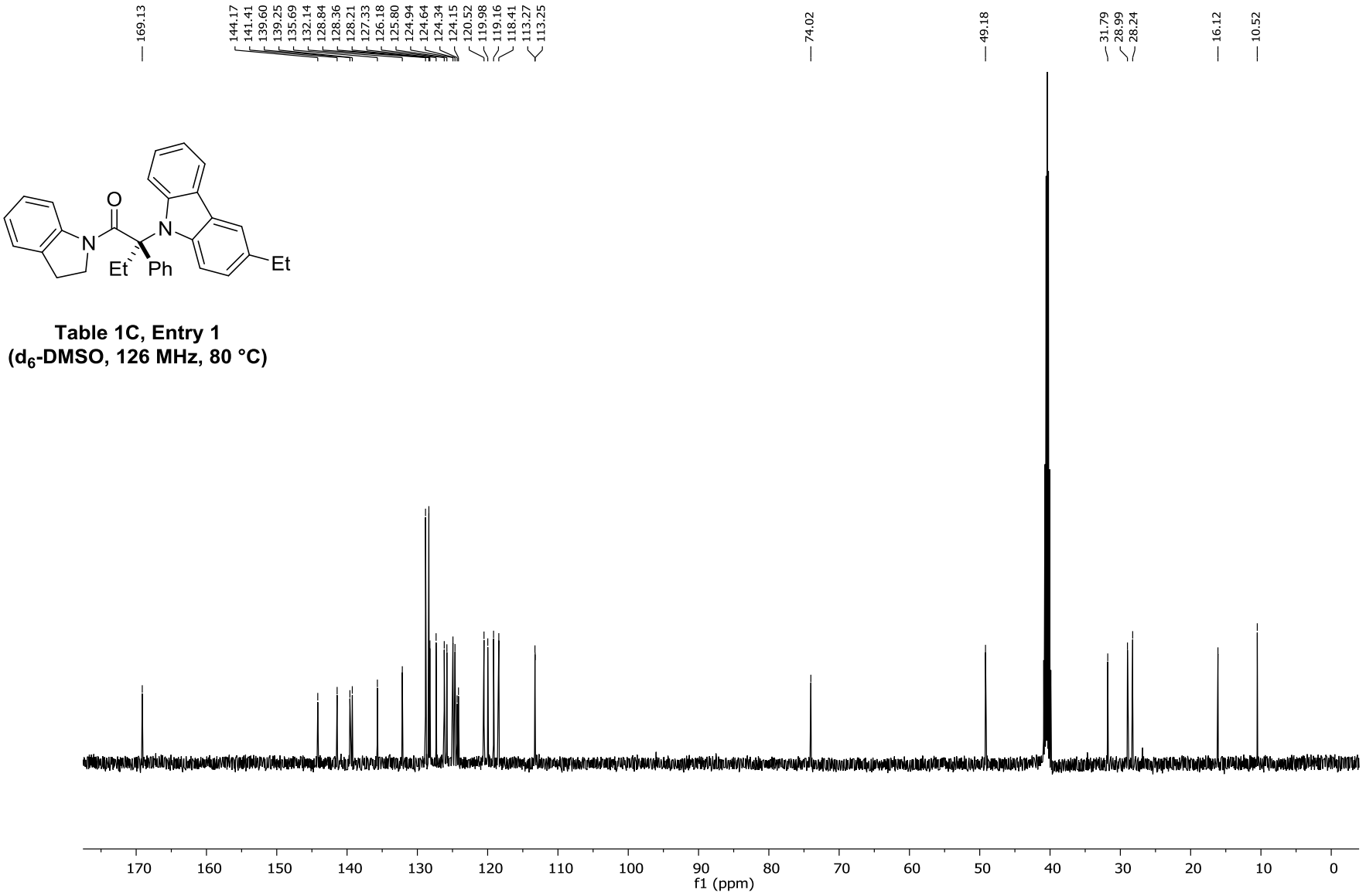


Table 1C, Entry 1
(d_6-DMSO, 126 MHz, 80 °C)

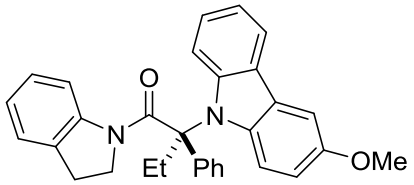


Table 1C, Entry 2
(d_6-DMSO, 500 MHz, 80 °C)

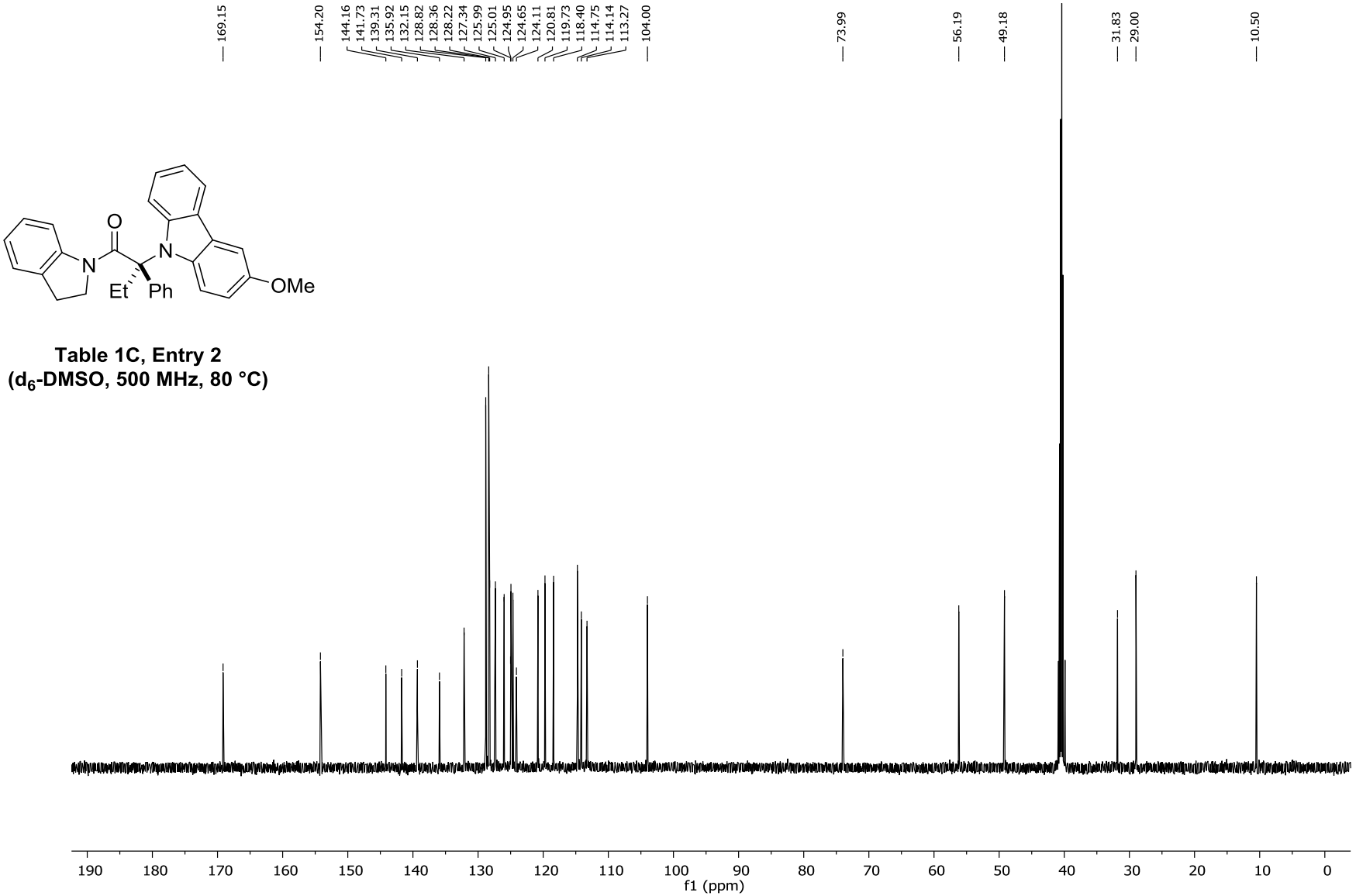


Table 1C, Entry 2
(d_6-DMSO, 500 MHz, 80 °C)

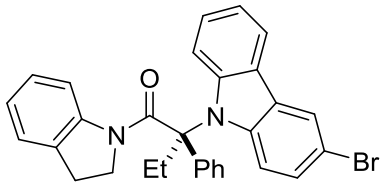
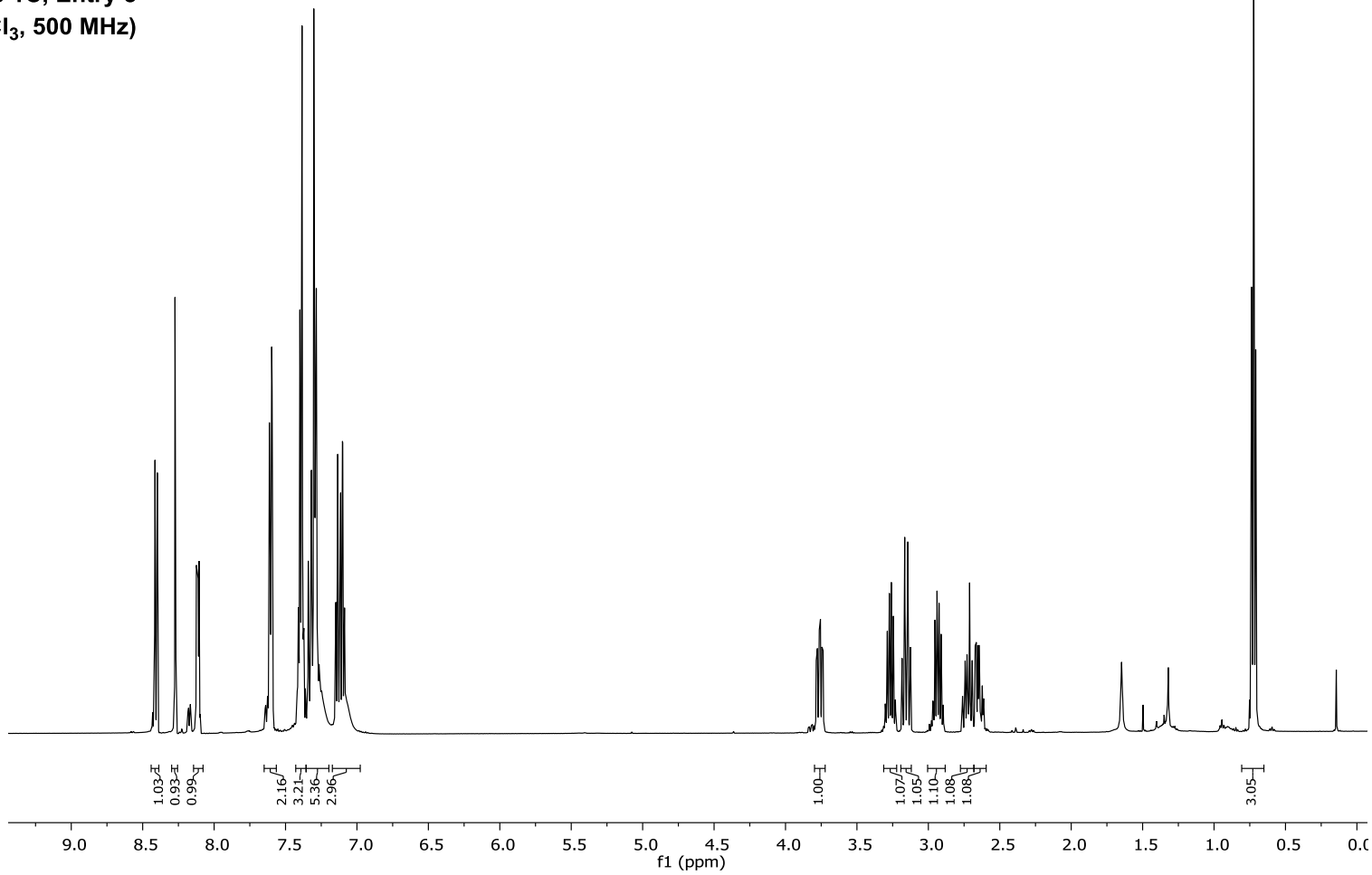


Table 1C, Entry 3
($CDCl_3$, 500 MHz)



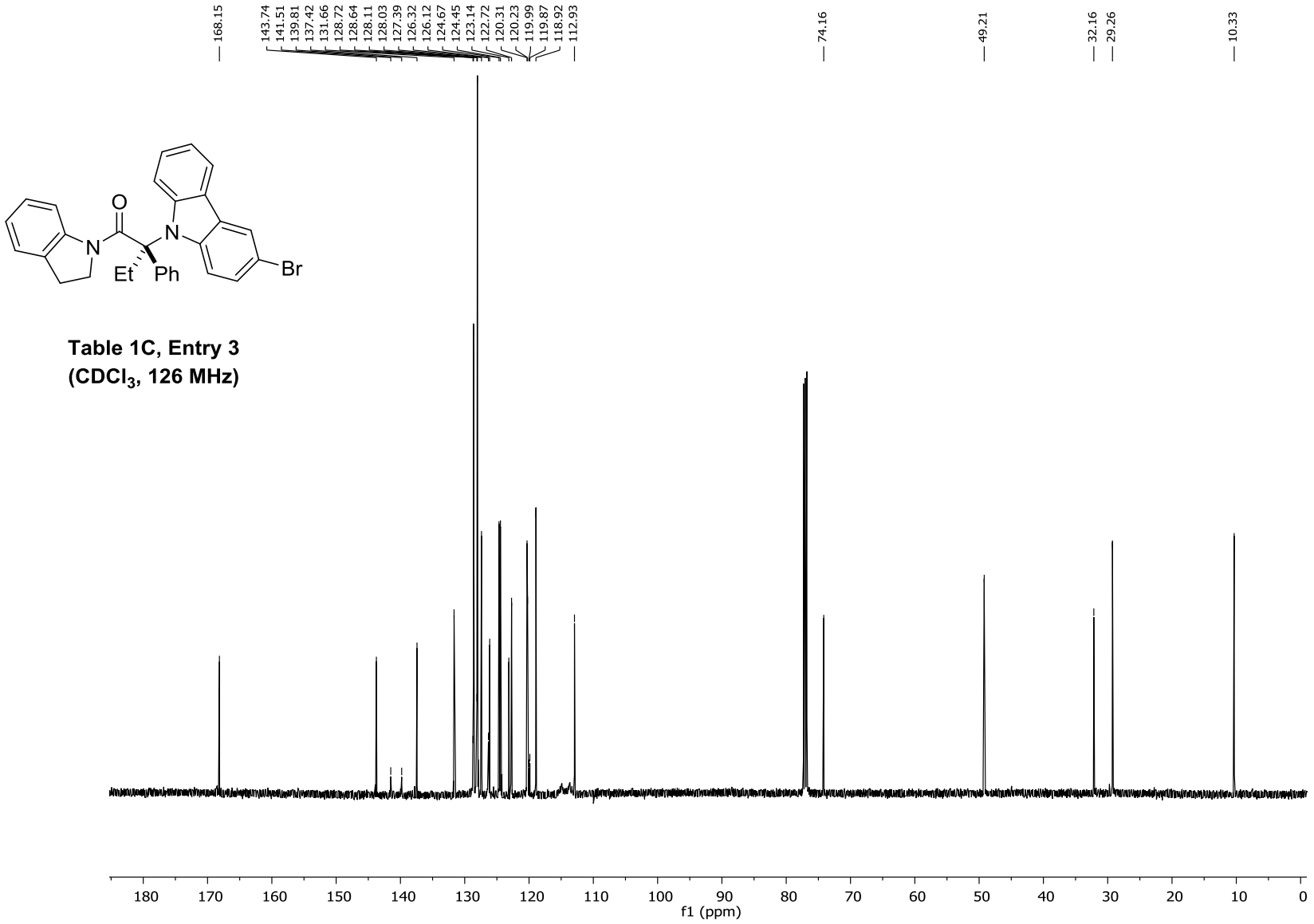


Table 1C, Entry 3
($CDCl_3$, 126 MHz)

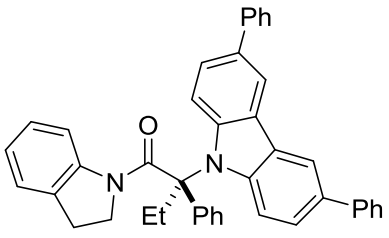
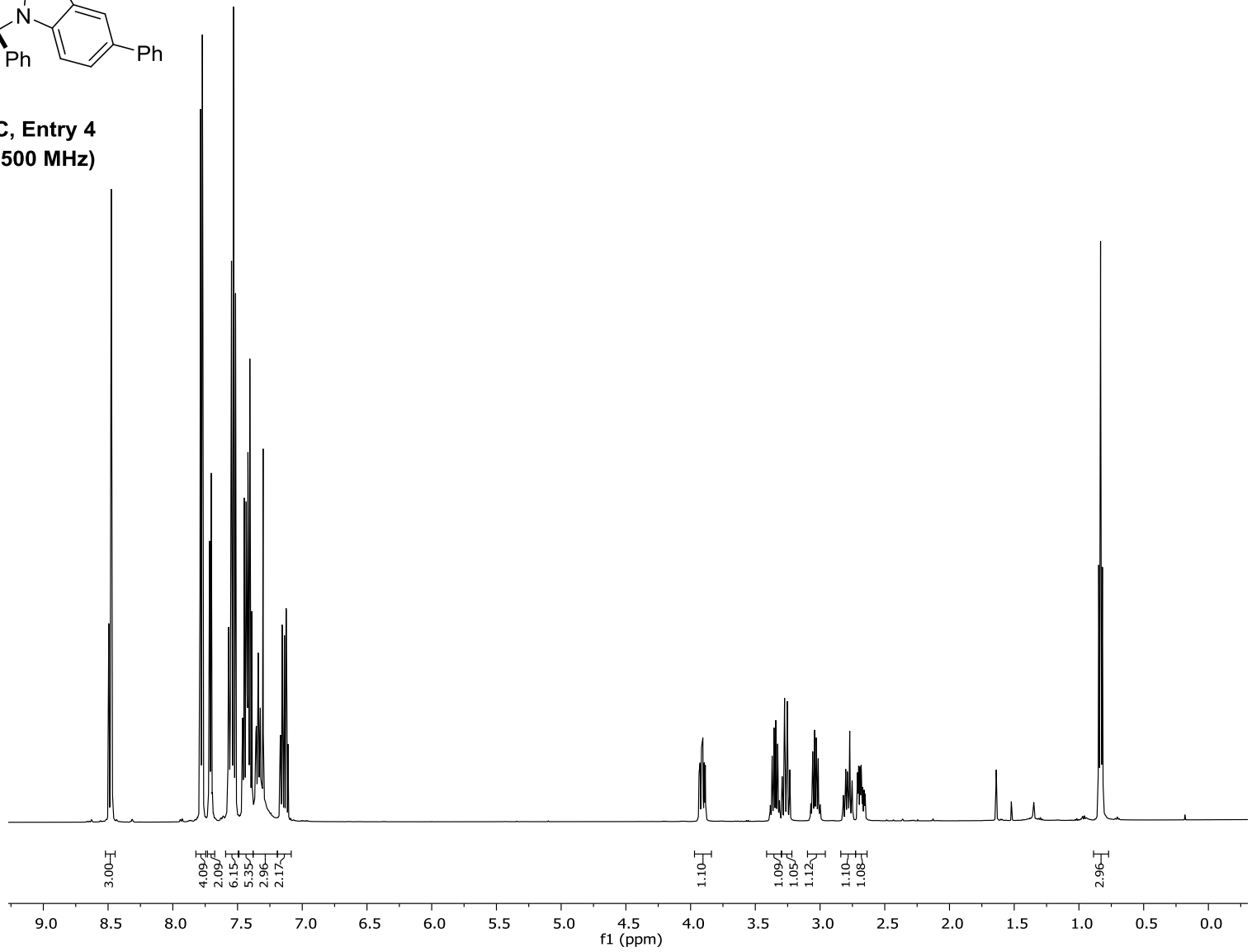


Table 1C, Entry 4
($CDCl_3$, 500 MHz)



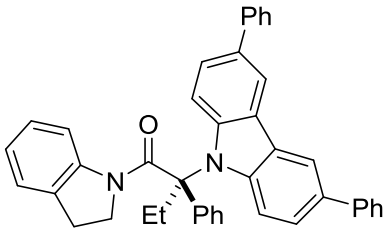


Table 1C, Entry 4
($CDCl_3$, 126 MHz)

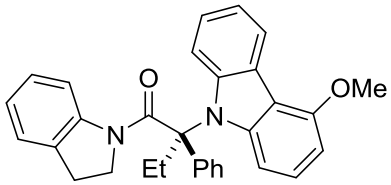


Table 1C, Entry 5
(d_6-DMSO, 500 MHz, 100 °C)

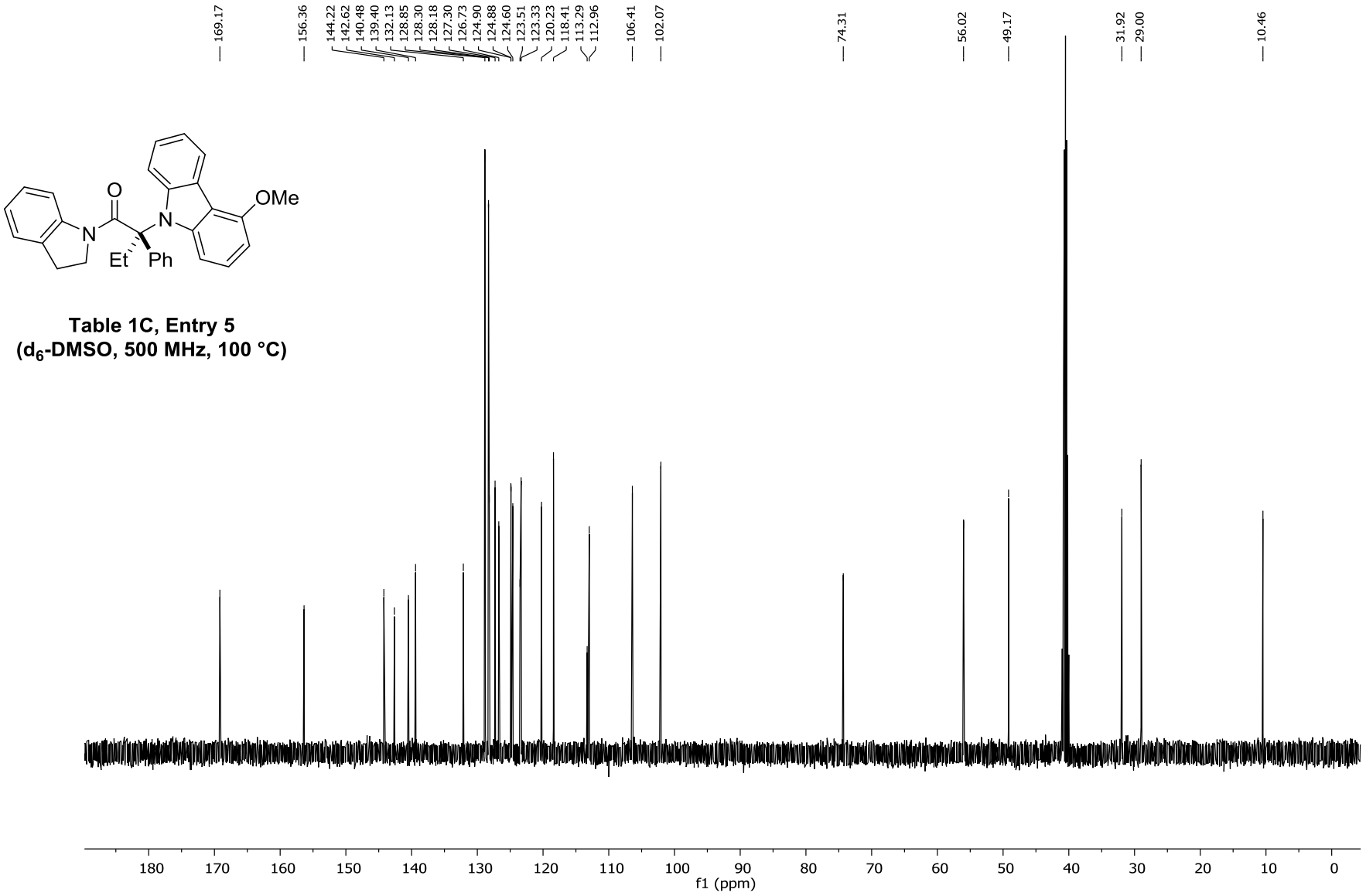


Table 1C, Entry 5
(d_6-DMSO, 500 MHz, 100 °C)

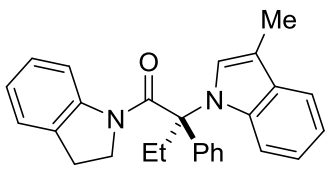


Table 1C, Entry 6
($CDCl_3$, 500 MHz)

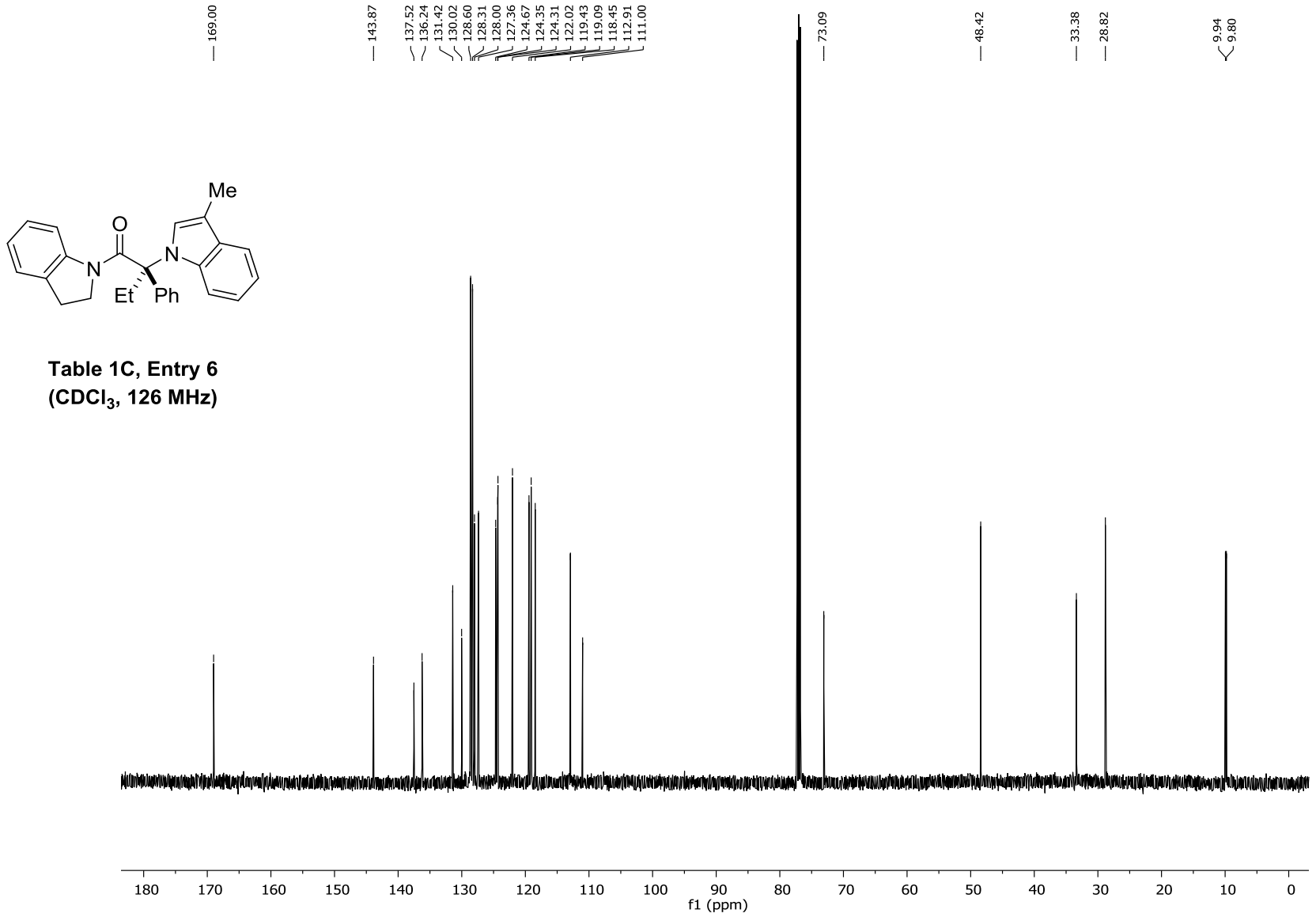


Table 1C, Entry 6
($CDCl_3$, 126 MHz)

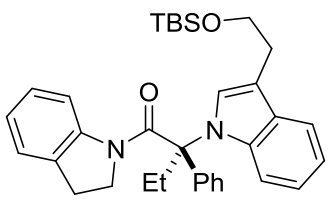


Table 1C, Entry 7
($CDCl_3$, 500 MHz)

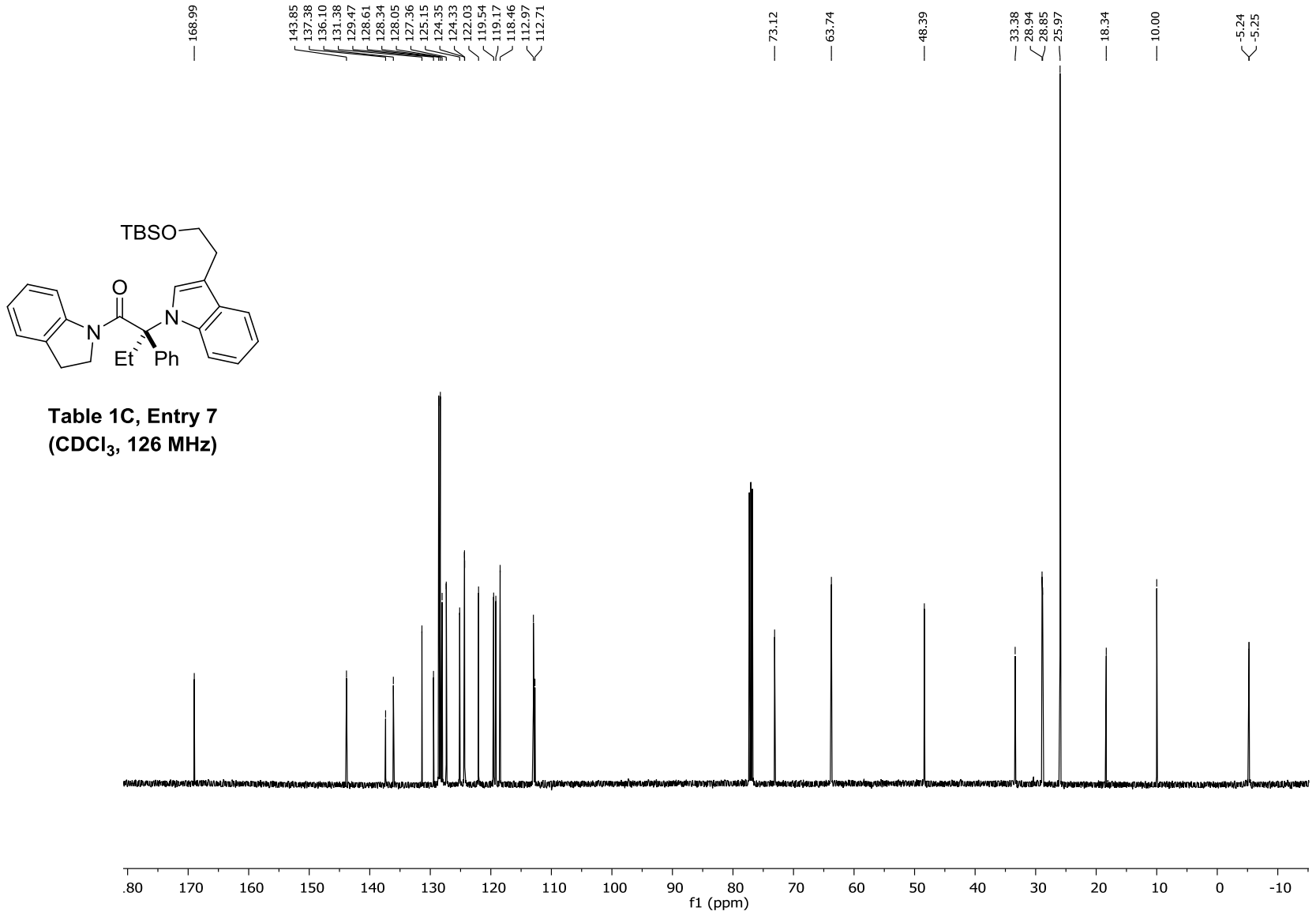


Table 1C, Entry 7
($CDCl_3$, 126 MHz)

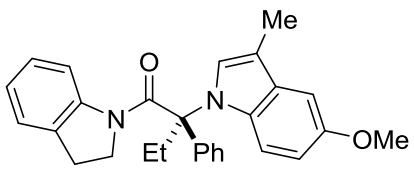


Table 1C, Entry 8
($CDCl_3$, 500 MHz)

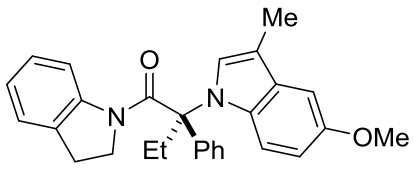


Table 1C, Entry 8
($CDCl_3$, 126 MHz)

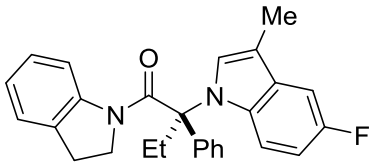


Table 1C, Entry 9
($CDCl_3$, 500 MHz)

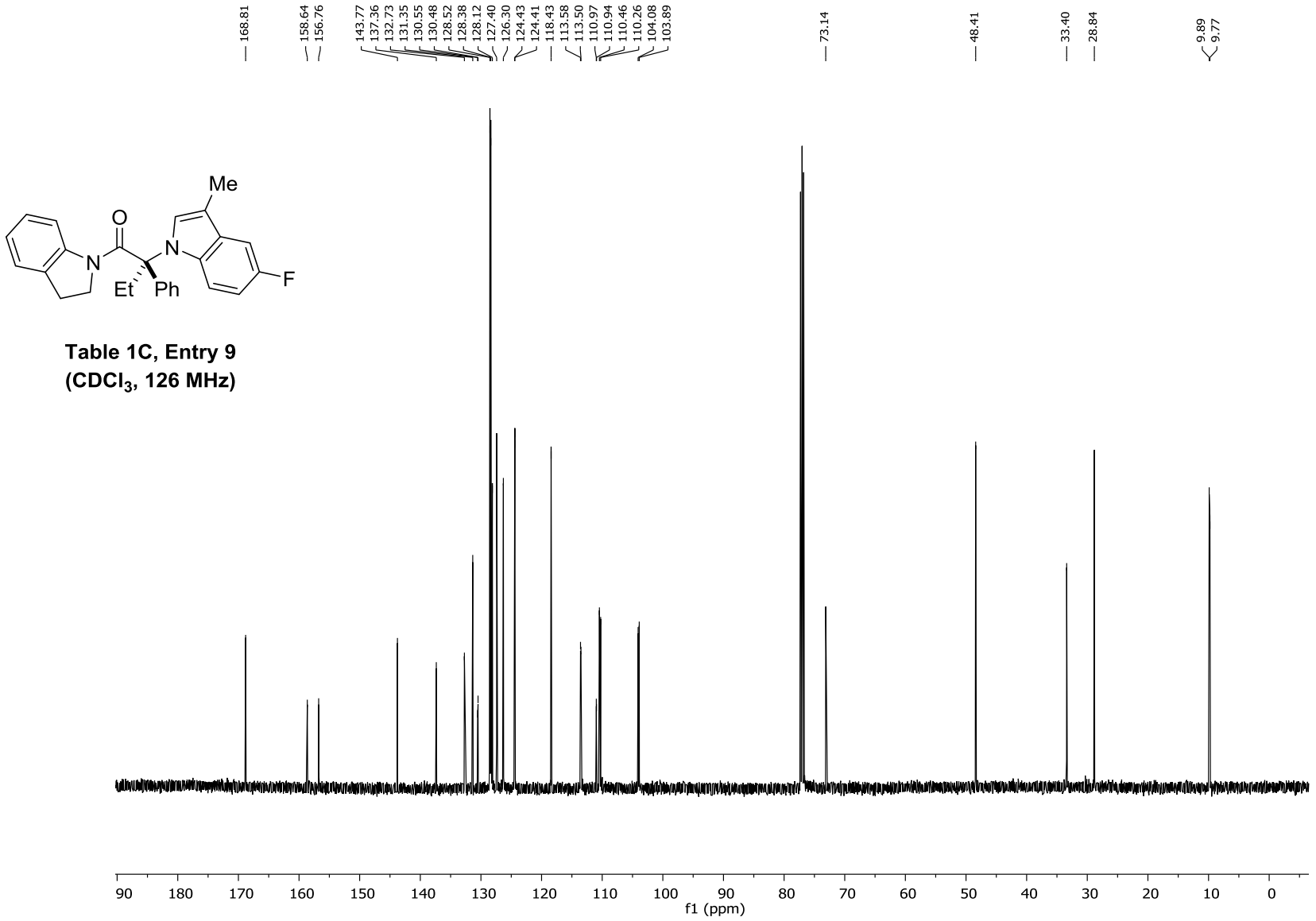
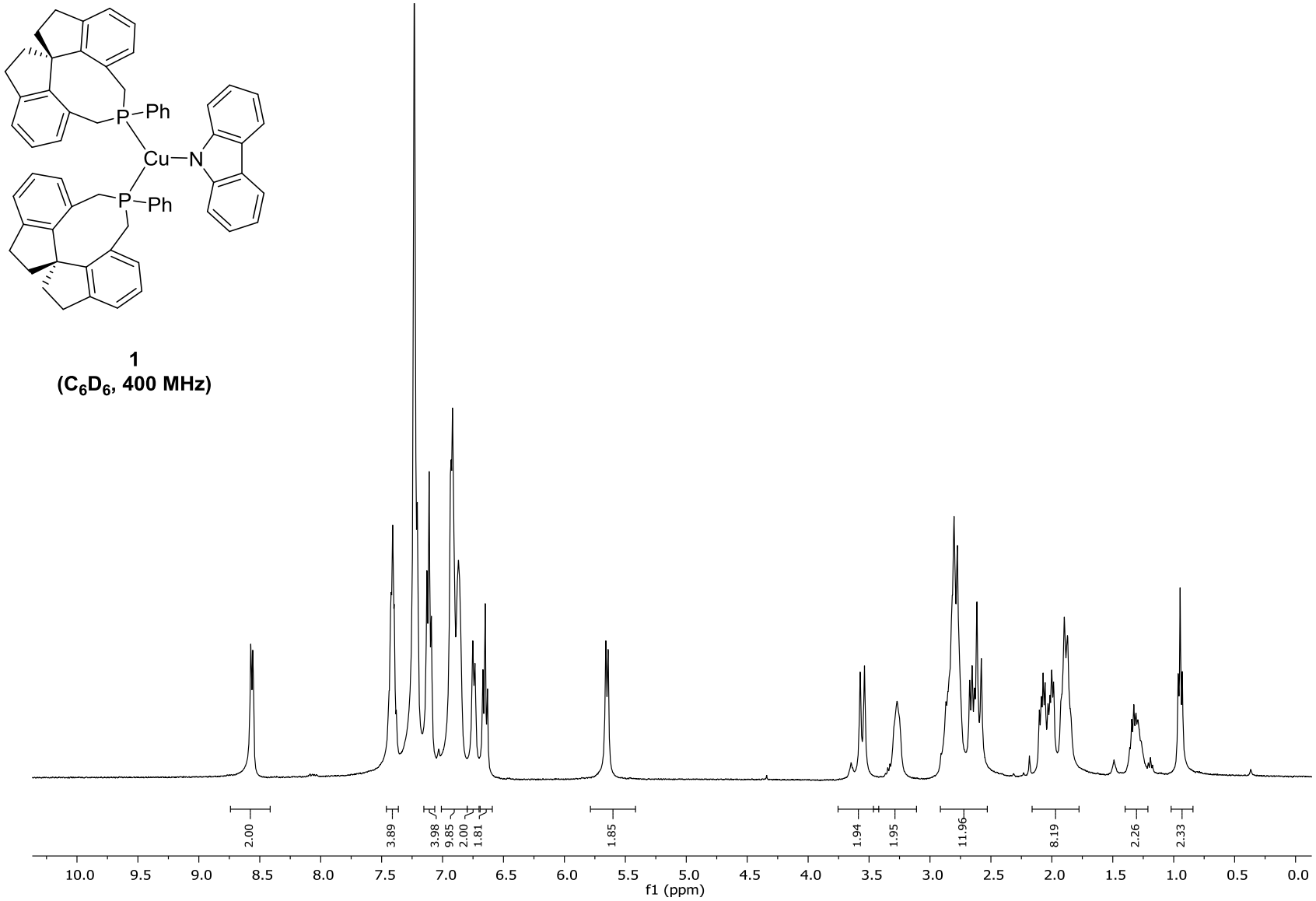
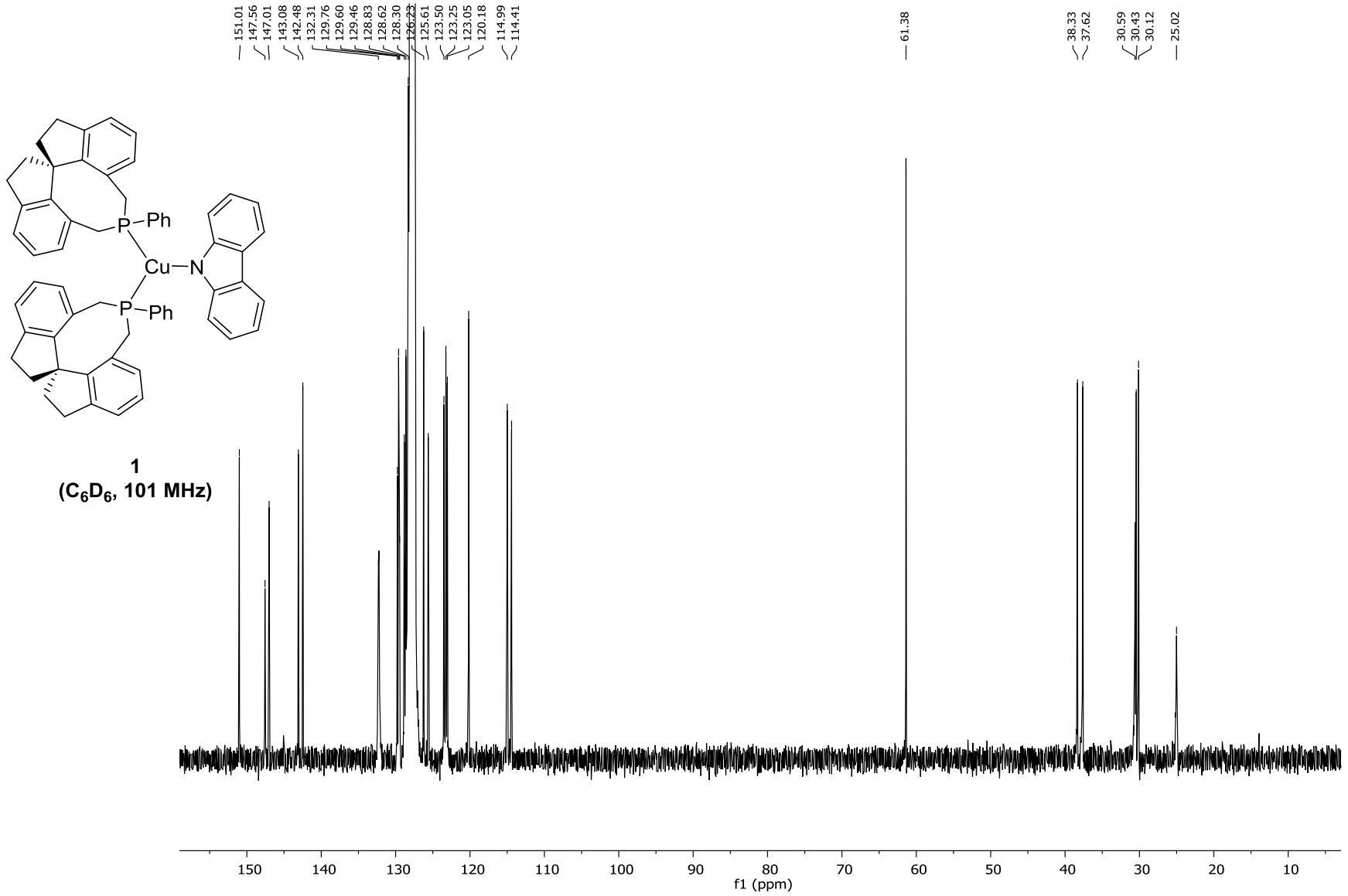


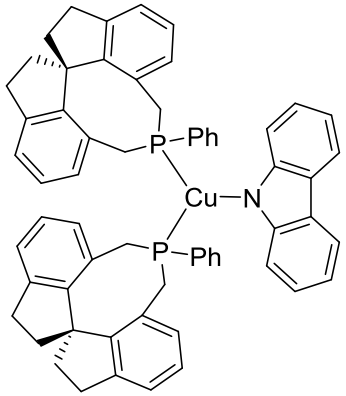
Table 1C, Entry 9
($CDCl_3$, 126 MHz)



1
(C_6D_6, 400 MHz)



1
(C_6D_6, 101 MHz)



1
(C_6D_6, 162 MHz)

REFERENCES AND NOTES

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